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LIQUID LASER RESEARCH

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SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND

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Quantum Chemistry Section
QUANTUM PHYSICS LABORATORY
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LIQUID LASER RESEARCH
FINAL REPORT

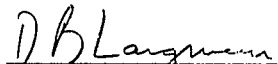
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FOREWORD

This report was prepared by the Quantum Physics Laboratory of Space Technology Laboratories, Inc., under USAF Contract No. AF-04(695)-97, for the Space Systems Division of Air Force Systems Command. The contract is monitored by Capt. R. D. Eaglet with the assistance of the Aerospace Corporation.

Research under this contract is being carried out in the Quantum Chemistry Section under the supervision of Dr. Maurice W. Windsor. The following persons have contributed to the research studies and to the preparation of this report: Dr. Maurice W. Windsor: Section Head and Project Manager; Dr. W. R. Dawson, Dr. J. L. Kropp, Mr. R. S. Moore and Mr. J. R. Novak, Members of the Technical Staff. Consultant services have been provided by Professor G. A. Crosby of the University of New Mexico. Technical support was provided by Mr. C. Krull, Mr. C. C. Stanley, by the STL Glass Shop and by the Research Division Model Shop. Secretarial assistance was rendered by Miss Ethel Dunn.

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ABSTRACT

The fundamentals of laser theory are reviewed and criteria are developed for laser action in the liquid state. What is needed are compounds which exhibit high-efficiency, narrow-line fluorescence of millisecond duration. Fluorescence of such long lifetime is usually completely quenched in solution by collisional deactivation of the excited molecule. Exceptions occur where the emitting level is well-shielded from the environment as in large organic molecules. The properties of several classes of such molecule are reviewed and thresholds for laser action are calculated. Rare-earth chelates appear to have the lowest thresholds and have been chosen for experimental studies as follows,

1. Fluorescence yields, lifetimes and emission spectra have been studied for several chelates as a function of solvent and temperature.
2. A high-intensity, 10,000 joule, laser test apparatus, employing a confocal resonant cavity with multiple-layer dielectric mirrors, has been constructed. This apparatus can be used for evaluation of liquid laser materials, either in liquid solutions or in rigid glasses, and at any temperature from room temperature down to 77°K.
3. Selected chelates of europium, terbium and samarium have been tested in the above apparatus as a function of solvent, concentration, temperature and flash energy.
4. In rigid glassy solvents at 77°K no laser action has been observed. At the higher flash energies, bubble formation and photochemical decomposition with the formation of particles of carbon present problems.
5. In fluid solutions at low temperatures (100 - 150°K) and high flash energies (8,500 joules), a few very recent experiments have yielded results which look like stimulated emission. However, without further experiments and demonstration of reproducibility, it is impossible to know whether these represent authentic laser action or not.

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I. Design for a Liquid Laser

A. Introduction

The feasibility of extending the maser principle to the optical region was first discussed by Schawlow and Townes (1) in December, 1958. Less than two years later in 1960, the first successful operation of a laser was reported by Maiman (2) using a crystal of ruby. Since that date, research activity in the laser field has been intense and in a period of less than three years, laser action has been reported in more than a dozen other crystals. In the majority of cases the emitting species is a rare-earth ion in a transparent crystalline host such as calcium fluoride or calcium tungstate. In addition to the solid-state lasers, gas lasers have been developed. The first to be described was based on a mixture of helium and neon (3). Since then laser action has been demonstrated in several other gaseous systems. The laser field is developing so rapidly that reviews are liable to be out of date before they get into print. However, for an excellent recent summary of the laser field see the review by Yariv and Gordon (4).

The remarkably short gestation period between conception and birth of the first laser, and the almost explosive growth of the laser field since then, would have been impossible but for one very important fact. This was the existence already of a vast body of information on the energy levels, luminescence and emissive properties of a wide range of inorganic materials. Nourished by this storehouse of knowledge of the properties of materials, the laser field has progressed by leaps and bounds. It is perhaps no coincidence that the majority of successful solid-state lasers so far have been based on rare-earth ions, whose emission spectra and energy levels have been extensively studied for almost half a century.

Despite its rapid growth, the laser field is still in its infancy. Further developments - extension of laser action to shorter wavelengths, to the liquid state, construction of higher-power lasers - may well require replenishment of the storehouse of fundamental knowledge in the materials sciences. Especially is this so in the realm of organic chemistry, which has contributed so much to other areas of technology in the last decade. Many classes of organic molecules exhibit luminescence. Generally the light emission is characteristic of the isolated molecule and involves energy levels which are well-shielded from the quenching effects of external perturbations. As a result, in many such molecules, fluorescence is seen not only in the vapor and pure crystalline state, but also in liquids and liquid solutions. Advantages of organic systems for laser application include the following,

1. Luminescence in all three phases.
2. The ability to vary the concentration of the active species over a wide range.
3. The almost unlimited number of organic molecules available by chemical substitution of successful basic structures, allowing a wide variation in frequency.
4. The possibility of molecular engineering or the tailoring of molecular structures for specific ends.

Certainly it is an exciting possibility to think of designing a specific molecule to perform a particular task. But to some extent in fields such as medicine, plastics and pest-control, this is already being done. In optics and spectroscopy the task is perhaps somewhat harder. Not all molecules emit light. Some are unstable. But then again certain classes emit light very efficiently and some organic molecules melt without decomposition at temperatures exceeding 500°C.

Many applications of lasers to military systems are likely to require that the laser generate continuous oscillations of relatively high power. This brings with it a severe cooling problem. Even with high efficiency materials, much of the enormous pump energy would appear as heat in the laser material. With a solid laser rod the cooling problem becomes more severe as the diameter increases, since the volume of material increases faster than the surface area through which heat can be removed. One promising possibility is to make the laser material liquid. Cooling could then be effected by pumping the working fluid through an external cooling system. There are, however, a number of obstacles to the successful construction of a laser device based on the use of liquids or fluid solutions,

1. Spectral lines are usually much broader in solution because of the perturbing effect of the constantly changing molecular environment.
2. Collisional quenching of fluorescence leads to non-radiative deactivation of the excited molecule, causing a marked drop in the quantum efficiency of fluorescence. This phenomenon is particularly marked for atoms and simple molecules of the inorganic type.
3. Finally, energy levels such as those employed in the ruby laser are not present in solution since they owe their existence to a splitting of normally degenerate levels of the chromium ion by the crystalline field of the host lattice.

In view of the above difficulties, it is clear that the successful construction of a liquid laser requires the exploitation of molecular systems, possessing intrinsic energy levels which are well-shielded from the quenching effects of external perturbations. The choice devolves logically onto the large class of polycyclic, organic molecules which contain extensively conjugated structures,

as exemplified by aromatic compounds and dye stuffs. In these molecules fluorescence is observable not only in the vapor and pure crystalline state but also in liquids and liquid solutions. Its insensitivity to external perturbations leads to the conclusion that, in these molecules, light absorption and fluorescence take place within the well-shielded systems of π -electrons, which are characteristic of this class of compound. The rare-earth chelates form a particularly favorable special class of the above type of molecule, in which the fluorescence of a central metallic ion is excited by absorption in the complex organic groups which surround and shield it from the environment.

The quest for a liquid laser (llaser) seems well worthwhile for many reasons in addition to those already mentioned. A liquid laser may potentially exhibit a number of other useful and advantageous properties not possessed by solid and gaseous systems. Among them are,

1. The ability to vary the concentration of the active species over a wide range.
2. Solvent-induced shifts of the energy levels, offering a mechanism for tuning the llaser by varying the solvent medium.
3. The use of energy transfer systems in which energy is absorbed by one component and then transferred to a second component whose subsequent fluorescence is then employed for lasering. This technique enables one to optimize the processes of absorption and emission independently of one another, thus promising an extremely efficient technique for population inversion in the emitting species.

B. Laser Fundamentals

We shall confine our remarks to 3-level systems and follow the treatment of Maiman(5). In a 3-level laser the stimulated emission takes place between the intermediate level 2 and the ground state (level 1). The processes are shown in Figure 1.

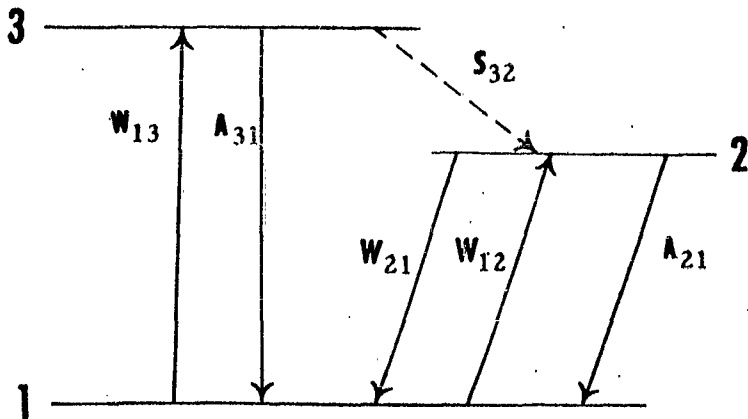


Figure 1 - Laser Energy Level Schematic

W_{21} is the induced probability of emission per unit time for the transition ($2 \rightarrow 1$) caused by the exciting radiation and W_{12} is the induced probability of absorption ($1 \rightarrow 2$). All absorption is of an induced nature since photons must be provided for absorption. However, in addition to induced emission there is also a probability for spontaneous emission given by the Einstein coefficient A_{21} . Since the rate of induced absorption and induced emission are given

respectively by $N_1 W_{12}$ and $N_2 W_{21}$, where N_1 and N_2 are the respective populations in the two states at photostationary equilibrium, it is clear that for a net excess of stimulated emission over absorption we must have $N_1 W_{12} > N_2 W_{21}$. The induced transition probabilities W_{12} and W_{21} are equal. Hence the condition for a net component of stimulated emission is simply,

$$N_2 > N_1 \quad (\text{I-I})$$

Thus in the 3-level laser it is necessary to provide enough incident radiation to pump more than 50% of the molecules out of the ground state and into level 2. In order to do this, molecules must first be pumped to a higher level 3, to which the transition probability from the ground state is large. Some of the molecules return by spontaneous emission A_{31} ; others pass by a radiationless process ($3 \rightarrow 2$) over to level 2. One can see intuitively that, in order to build up a sizable population in level 2, the spontaneous transition probability A_{21} must be small compared to W_{13} and S_{32} . Under these circumstances the population in level 2 builds up until the number of molecules entering state 2 per second from 3 is equal to the number leaving by spontaneous emission to the ground state. If the quantum yield of the cross-over process is high $S_{32} \gg A_{31}$ and we can neglect A_{31} . At the photostationary equilibrium we then have

$$\frac{dN_1}{dt} = 0 = -N_1(W_{13} + W_{12}) + N_2(A_{21} + W_{21}) \quad (\text{I-2})$$

$$\frac{N_2}{N_1} = \frac{W_{13} + W_{12}}{A_{21} + W_{21}} \quad (\text{I-3})$$

Applying the condition $N_2 > N_1$ and remembering that $W_{12} = W_{21}$ we get,

$$W_{13} > A_{21} \quad (I-4)$$

as the condition for net stimulated emission. An electromagnetic wave travelling through a medium in which the above condition is satisfied would be coherently amplified rather than attenuated by net absorption as is usually the case. Unless the medium be infinite in extent subsidiary conditions arise because of boundary effects. A practical laser device usually takes the form of a tubular piece of the active material bounded at each end by parallel mirrors of high reflectivity at the laser operating frequency. At each reflection the energy of the electromagnetic wave is reduced by a factor r , where r is the reflection coefficient. This leads to the further requirement that the amplification of the wave during transit between the end-plates exceed the attenuation caused by reflection. This condition must be met if useful amplification or self-oscillation (which amounts to continued amplification of a photon which arises by spontaneous emission) is to be achieved.

The equation for the attenuated intensity I_t of a beam of light of initial intensity I_0 on traversing a medium of length l of decadic absorption coefficient β is

$$I_t = I_0 10^{-\beta l} \quad (I-5)$$

The absorption coefficient is given by the population difference times the intrinsic strength or extinction coefficient of the transition,

$$\beta = (c_1 - c_2) \epsilon \quad (I-6)$$

Here, in anticipation of the analysis to follow for the metastable states of organic molecules, we have used the customary symbols c for

concentration in gm moles per litre and ϵ for the molar decadic extinction coefficient. Population inversion with $c_2 > c_1$ causes β to become negative. Hence the exponent in Eq. (I-5) is positive and instead of attenuation we get amplification. Thus for continued amplification as the wave is reflected back and forth we must have,

$$10^{-\beta l} r \geq 1 \quad (I-7)$$

Since usually $\beta l \ll 1$, we can replace $10^{-\beta l}$ by $(1 - \beta l \log_e 10)$. Making this approximation and bearing in mind that r is close to unity, we obtain the condition for oscillation as,

$$-\beta l = \frac{1}{2.3} \frac{1-r}{r} \approx \frac{1-r}{2.3} \quad (I-8)$$

or using Eq. (I-6) and putting $(c_1 - c_2) = -\Delta c$,

$$\epsilon l \Delta c = \frac{1-r}{2.3} \quad (I-9)$$

Thus, expressed in words, the two basic criteria for laser action become,

- 1) There must be more molecules in the upper state than in the ground state.
- 2) The product of the population difference, extinction coefficient and path-length must be such that the amplification factor $10^{\epsilon l \Delta c}$ more than offsets reflection losses at the end-plates.

The factors ϵ , l and Δc are not independent of each other. The transition probability A_{21} is proportional to the integrated absorption coefficient $\int \epsilon_\nu d\nu$ where ϵ_ν is integrated over

the width of the absorption band. For a given light intensity it is easier to achieve population inversion for systems in which A_{21} is small, corresponding to a forbidden transition $2 \rightarrow 1$. However, this also means that ϵ is small and a greater length of material will be needed to offset reflection losses. In practice it turns out that most transitions of interest for potential laser application will have values of A_{21} lying between 10^6 sec^{-1} and 10^2 sec^{-1} . Since the mean lifetime of the upper state is $\tau_{21} = 1/A_{21}$, this corresponds to fluorescent lifetimes in the range 10^{-6} to 10^{-2} sec.

Another factor becomes important at the short lifetime end of the range. Since the transition is relatively strong, Δc need have only a small absolute value to satisfy condition 2 even for quite modest path lengths (~ 10 cm). In principle, therefore, a low initial ground-state concentration of molecules would suffice. However, unless the pumping transition has a very high absorption coefficient (large A_{31}), it is difficult to get the system to absorb the required amount of light i.e. the sample is optically very thin. Later we shall discuss ways of getting around this difficulty for organic systems. Nevertheless a useful third criterion is,

- 3) The absorption coefficient for the pumping transition shall be as high as possible.

It is better if the absorption covers a broad band of wavelengths since this leads to more efficient use of the exciting light.

Finally, it is not so much the total oscillator strength f which determines the ease with which the system will laser but the differential strength $df/d\nu$. Since $f \propto \int \epsilon_\nu d\nu$, we have $df/d\nu \propto \epsilon_\nu$. This leads to the fourth criterion;

- 4) The peak extinction coefficient should be as high as possible. Thus for a given oscillator strength a molecule in which the emission is concentrated into a narrow frequency band is preferable to one with a broad emission spectrum. If several bands exist, the most intense will be favored for laser action.

C. Luminescence in the Liquid State

While the majority of atoms and molecules exhibit fluorescence in the gas phase at low pressure, this fluorescence is usually completely quenched in liquid solutions owing to rapid, collisional deactivation of the excited species. It is thus necessary to search for systems in which the fluorescent transition is well-shielded from the effects of external perturbations, such as arise from the constant jostling of neighboring molecules in the liquid state. In addition, such perturbations, even in cases where fluorescence is not completely quenched, lead to broadening of the energy levels. This effectively spreads the total oscillator strength over a wider band of frequencies, thus making it more difficult to satisfy the amplification condition at any one frequency.

Finally, in many cases, such as ruby, the energy levels employed in the solid state laser are not present in solution since they owe their existence to the splitting of normally degenerate levels of the chromium ion by the crystalline field of the host lattice.

The difficulties outlined above lead one to a consideration of molecular systems which possess well-shielded, intrinsic fluorescent levels. The choice devolves logically on to the large class of complex, organic molecules which contain extensively conjugated structures. In these molecules fluorescence is observable not only in the vapor, and pure crystalline state but also in liquids

and liquid solutions. Perhaps most promising of all are the organic rare-earth chelates. These offer the especial advantage that the pumping transition is a broad band characteristic of the organic part of the complex whereas, even in solution, the fluorescence is the characteristic narrow emission of the central rare-earth ion. Several other classes of compound exist in which a metallic ion is complexed by one or more large organic groups. However, little is as yet known about the spectroscopic properties of these compounds. The luminescent properties of the rare-earth chelates, on the other hand, have been studied in some detail which makes them a logical first choice for laser studies. This subject is reviewed in the next section.

II. Selection of Materials

A. Possible Luminescent Compounds

There are several classes of luminescent compound that present themselves for evaluation.

1. Fluorescent States of Aromatic Molecules

This class comprises polycyclic aromatic hydrocarbons such as naphthalene, anthracene and their derivatives.

The basic energy level diagram for such molecules is shown in Figure 2. The lowest excited singlet state S_1 is responsible for fluorescence and can be reached by light absorption either directly or via absorption first to S_2 followed by a radiationless drop to S_1 . The latter process is highly efficient and the system thus has the required succession of levels for a 3-level laser. However, fluorescent lifetimes for these compounds lie typically in the range 10^{-6} to 10^{-9} sec., and overall band widths of the emission are of the order of 1000cm^{-1} . As a result very high pumping rates would be needed to obtain population inversion for these materials.

2. Triplet States

A further factor to be considered in evaluating aromatic compounds for laser application is the existence of another level between S_1 and the ground state. This level is the lowest triplet state T_1 and is reached by radiationless transition from S_1 . Despite the reversal of electron spin which must occur on crossing to the triplet state, the cross-over takes place with surprisingly high efficiency and competes effectively with the normal fluorescence $S_1 \rightarrow S_0$. The triplet state gives rise to phosphorescence or afterglow. Because of the multiplicity selection rule of quantum mechanics, the process is "forbidden". Phosphorescence lifetimes usually lie in the range 10^{-6} to 10^1 sec. and total band widths of the emission are again of the order of 1000cm^{-1} (6).

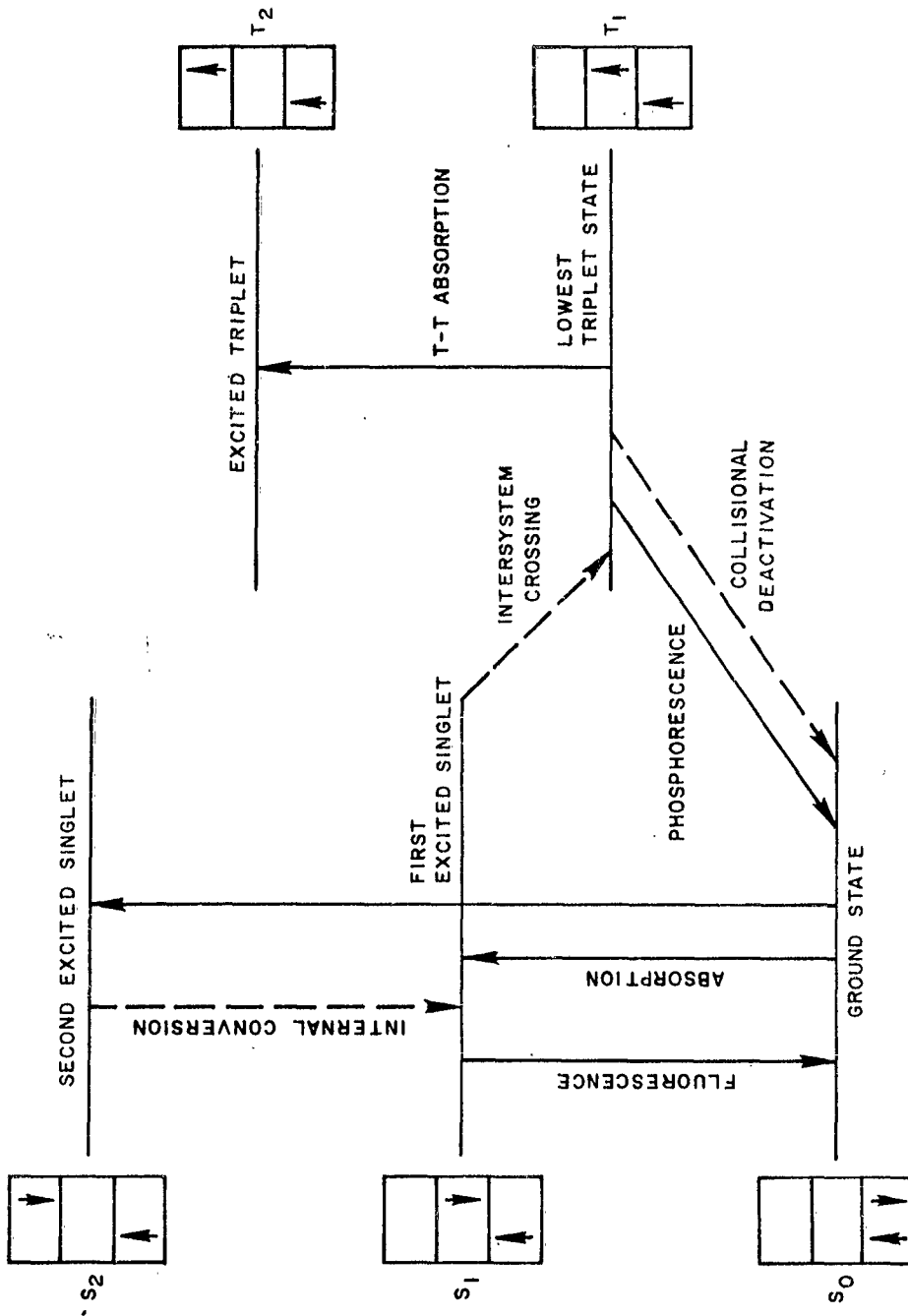


Figure 2 - Formation and Deactivation of the Triplet State in Complex Molecules. Arrows in the boxes indicate electron spin.

Population inversion for the triplet state has been reported by Porter and Windsor (7) in flash photolysis experiments on the triplet-triplet absorption of tetracene, pentacene and several other compounds in solution. Unfortunately, owing to its long radiative lifetime, phosphorescence is often completely quenched in fluid solvents. However, in halogen substituted compounds and in such compounds as biacetyl, where spin-orbit coupling enhances the strength of the $T_1 \rightarrow S_0$ transition, phosphorescence has been observed in solution. In these compounds, also again by reason of spin-orbit coupling, the quantum efficiency of conversion to the triplet state approaches 100%. In view of these facts it is apparent that phosphorescence and triplet states should not be neglected in the search for materials for application in a liquid laser. Examples which may be suitable for laser application are given in Table I.

3. Rare-earth Chelates

In these compounds a central rare-earth ion is surrounded by three large organic groups to form a complex molecule. Crosby and coworkers (8,9,10) have made detailed studies of energy transfer in these molecules. They combine the advantages of broad absorption bands characteristic of the organic groups with narrow line-like emission characteristic of the rare-earth ion. In addition, fluorescence lifetimes are in the millisecond range and several compounds exhibit appreciable fluorescence even in liquid solutions. The area where information is most lacking is that of quantum yields.

4. Other Metal-Organic Compounds

Several other classes of compound exist in which a metal ion is complexed by one or more organic groups. These include the porphyrins and phthalocyanines and the metal compounds of cyclopentadiene. Luminescence studies of several metal porphyrins have been made (11) but, to our knowledge, no one has yet prepared any rare-earth porphyrins. All of the rare-earth cyclopentadienides have been prepared (12,13), but virtually no spectroscopic studies

TABLE I
COMPOUNDS WHOSE TRIPLET STATES
SHOW LASER POTENTIAL (14,15)

<u>Compound</u>	<u>Quantum Yield</u>	<u>Lifetime sec.</u>	<u>Frequency cm⁻¹</u>
Acetophenone	0.44	8×10^{-3}	26,000
Benzophenone	0.50	6×10^{-3}	24,400
Bromobenzene	--	10^{-4}	
P-dibromobenzene	--	3×10^{-4}	
B-Iodonaphthalene	--	2.5×10^{-3}	19,000

and no luminescence work whatsoever have been made on these interesting compounds. Here is a potentially fruitful area for further work but, until materials studies have been made, these compounds present too many unknowns to warrant consideration for possible laser applications.

B. Calculation of Thresholds for Lasering

The minimum excess concentration of excited states needed to provide enough stimulated emission to offset losses and allow laser action to ensue can be calculated using the following formulae from the paper by Yariv and Gordon (4). The required excess concentration $\Delta n_c/v$ is given by,

$$\frac{\Delta n_c}{v} \geq \frac{4\pi^2 \bar{\nu}^2 \Delta \bar{\nu}}{c^3} \cdot \frac{t_s}{t_p} \quad -7$$

where
$$t_p = \frac{L}{\alpha c} = \frac{Q}{2\pi \bar{\nu}} \quad -8$$

The various losses in the cavity such as transmission and absorption in the mirrors, scattering in the optical medium, diffraction because of the finite size of the mirrors, are characterized by a single parameter, t_p , which is the time constant for the decay of radiation in the cavity. It is simply related to the length L and the total loss per pass α or to the conventional quality factor Q as in the above equation. t_s is the spontaneous radiative lifetime of the emitting state. Substituting for t_p in equation 7 and converting from frequency ν to wave-number $\bar{\nu}$ by putting $\nu = c\bar{\nu}$ we obtain,

$$\frac{\Delta n_c}{v} = \frac{4\pi^2 \bar{\nu}^2 \Delta \bar{\nu} t_s \alpha c}{L} \quad -9$$

Using the following values, $c = 3 \times 10^{10}$ cm/sec

$$\alpha = 0.02$$

$$\bar{\nu} = 20,000 \text{ cm}^{-1} \text{ (5000\AA)}$$

$$L = 10 \text{ cm}$$

$$\text{we get, } \frac{\Delta n_c}{V} = 0.96 \times 10^{18} \Delta \bar{\nu} \cdot t_s \text{ cm}^{-3} \quad -10$$

If we divide by Avogadro's number, 6×10^{23} , and multiply by 1000, we obtain the critical concentration excess Δc gm moles/litre,

$$\Delta c = 1.6 \times 10^{-3} \Delta \bar{\nu} \cdot t_s \text{ gm moles/litre}$$

In Table II we give the critical concentration excess required for laser action for the several classes of materials mentioned above, together with that for ruby for the purpose of comparison. We see that the rare-earth chelates have the lowest threshold and are therefore the favored candidates for demonstration of laser action in liquid solutions. For these molecules, using a 10cm long cell, a concentration excess of a few times 10^{-4} Molar should suffice. Accordingly several chelates have been chosen for experimental evaluation in our laser test apparatus. The experiments are described in Section VIII. Because of their high thresholds, it would probably be necessary to increase the cavity length to 100cm for the triplet states. Making the cell this long however, presents numerous problems of practical design and also reduces the chances of maintaining a low-loss optical path between the end-mirrors. For these reasons it was decided to focus attention mainly on the chelates.

C. Selection of Particular Chelates

A very large number of organic chelating agents are known (17). Since these have widely differing spectral absorption properties, it is in principle possible to vary the absorption

TABLE II

LASERING THRESHOLDS FOR VARIOUS MATERIALS

Compound	$\Delta\nu$ cm ⁻¹	t_s secs	Δc gm moles/litre	Pumping rate P Einsteins/litre sec
Ruby	10	3×10^{-3}	4.8×10^{-5}	1.6×10^{-2}
Chelates	200	1×10^{-3}	3.2×10^{-4}	3.2×10^{-1}
Triplet States (Aromatic ketones)	1000	10^{-2}	1.6×10^{-2}	1.6
Triplet States (Aromatic Hydrocarbons)	1000	1	1.6	1.6

and emission characteristics of the chelate independently of one another. To begin with, however, it is important to select chelates about which something is already known spectroscopically. Intramolecular energy transfer in rare-earth chelates was first reported by Weissmann (18) for complexes of europium and later by Sevchenko and Trofimov (19) who studied chelates of europium, samarium and terbium. Crosby, Whan and Alire (9) recently reported studies on chelates of the tripositive ions of La, Sm, Eu, Gd, Tb, Dy, Tm, Yb and Lu. These experiments indicate that the efficiency of energy transfer depends on the relative positions of the resonance energy levels of the rare-earth ions and the metastable triplet states of the complexes.

In order for the rare-earth ion fluorescence to be excited, it is necessary that the lowest triplet state of the complex lie above the emitting level of the ion. In Crosby's work, luminescence spectra were recorded for the benzoylacetates (MB_3) and the dibenzoyl-methides, (MD_3), structural formulae for which are given in Figures 3 and 4 . Only the compounds of Eu, Tb, Dy, Sm showed appreciable line emission characteristic of the rare-earth ion. The molecular emission (phosphorescence and fluorescence) from these compounds was negligible by comparison. Both the B_3 and D_3 compounds of Eu^{3+} and Tb^{3+} were especially bright emitters; DyB_3 was slightly weaker and the two chelates of Sm^{3+} showed less intense but still clearly visible lines. The absence of line emission from DyD_3 is explained by the fact that the lowest triplet state of the D_3 complex falls below the Dy^{3+} resonance level.

Guided by Crosby's previous work and by his advice as consultant to our research program, we decided to select the benzoylacetates and dibenzoylmethides of europium and terbium for initial investigations. As the work progressed we decided to examine also the acetyl acetates and the thienoyl-trifluoro-acetyl-acetates of these ions. We refer to these as MA_3 and $M(TTA)_3$ respectively

where M stands for the metal ions. These compounds were synthesised either by Professor Crosby or by ourselves as outlined in Section IV.

The most pressing need was for reliable data on the quantum yields of fluorescence. We therefore decided to measure the quantum yields of the above compounds as a function of solvent and temperature. This work is described in Section VI. It is important to choose a compound with a high quantum yield since this minimises the required pumping energy and also results in less heating of the liquid laser solution.

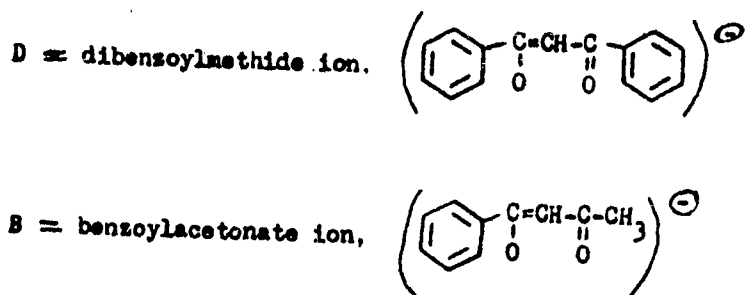
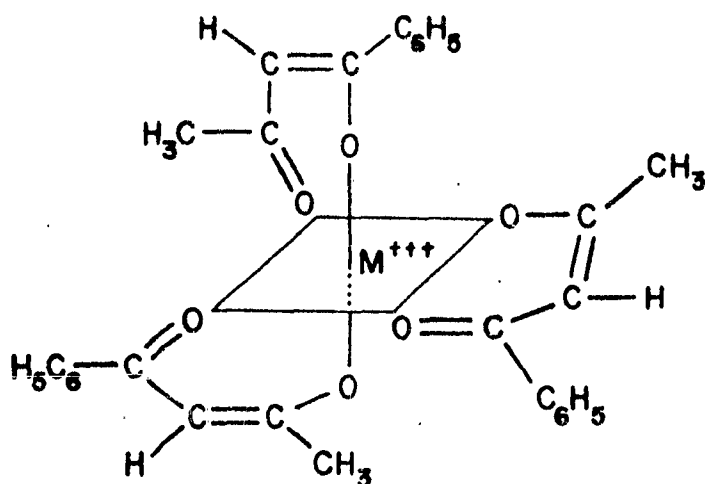


Figure 3. Formulae for dibenzoylmethide and benzoylacetate



and

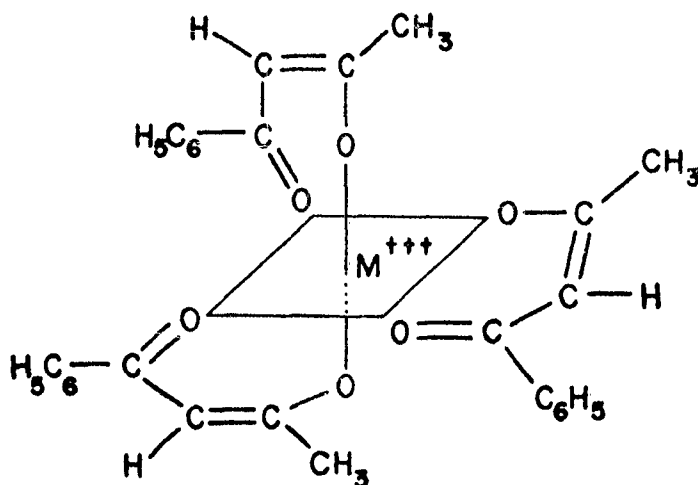


Figure 4. Two Possible Structural Formulae of the Trisbenzoyl-acetonate Chelate of a Trivalent Rare-Earth Ion.

D. Pumping Considerations

This brings us to a discussion of the light intensities needed to produce the required excess concentrations in the emitting state. The minimum pumping rate for a 4-level laser is,

$$P = \frac{\Delta c}{\phi \tau_s}$$

where ϕ is the quantum yield of the emission process. Values of P are given in the last column of Table II. Let us compare these figures with those obtainable with current light sources. The helical flash lamps in present use at STL are similar to those for which Christie and Porter (20) reported 1.18×10^{20} quanta of average wavelength 3400Å absorbed by a uranyl oxalate actinometer solution with an input energy of 2700 joules. Since they assumed 40% absorption of the exciting light, the actual output in the region of uranyl oxalate absorption (2000 - 4900Å) was 3×10^{20} quanta. The duration of their flash was about 1msec, so the light intensity was 3×10^{23} quanta/sec or 0.5 Einsteins/sec., where an Einstein is equal to Avogadro's number of quanta or "1 gm-mole of quanta". At STL, input energies up to 12,000 joules have been used. We can assume then that the available light intensity is about 2 E/sec. With a cell 10cm long and 1cm^2 cross-section, this corresponds to an excitation rate of 200 E/litre sec. Intensities of 1200 E/litre sec have been reported by Claesson and Lindqvist (21) using an annular flash lamp 8cm long with an input energy of 7,500 joules. However, the flash duration was only 17μsec.

We see that for the chelates the pumping rates available with present flash lamps are several hundred times greater than the minimum rate given in the last column of Table II. This is fortunate, since it permits somewhat inefficient use of the pumping light as is likely to occur when using a concentrated chelate solution as discussed in Section VIII A.

III. Summary of the Research Program

A. Rationale and Plan of Attack

Our attempts to develop a liquid laser have been based on the following rationale,

1. A liquid laser requires a material which exhibits high-efficiency, narrow-line fluorescence of about 1 millisecond lifetime even in solution.

2. Since fluorescence of long life is often completely quenched by collisional processes in solution, these properties demand a compound with emitting levels that are well-shielded from the environment, Rare-earth chelates seem to be the optimum choice.

3. Reliable data on quantum yields of fluorescence for these compounds are of paramount importance but are very scarce. It is therefore important to construct apparatus and make quantum yield measurements.

4. Studies of emission spectra and lifetime measurements are also important. However, by courtesy of our consultant, Professor Crosby, we have rapid and timely access to such data from his research program. It is, therefore, necessary to make such studies for only a few new compounds.

5. Since stimulated emission has not yet (February 1962) been observed for rare-earth chelates, a logical approach is to first search for laser action under optimum conditions (low temperature, rigid medium) and then to relax these requirements in a controlled manner, i.e.,

- a. low-temperature, rigid glass
- b. low-temperature liquid
- c. room-temperature liquid

In this way molecules with the greatest propensity for liquid laser action will be uncovered with the maximum economy of effort.

B. Summary of Results

1. Samples of many rare-earth chelates have been obtained from Professor Crosby. A few chelates were synthesised in our own laboratory. Based on Crosby's work, emphasis has been placed on chelates of europium and terbium.

2. Experimental apparatus for accurate measurement of quantum yields of fluorescence has been constructed. Measurements have been made for several europium and terbium chelates in a variety of solvents, both at room temperature and at low temperatures down as far as 77°K . One chelate, Terbium Acetylacetonate, gives the remarkably high yield of 32% even in solution at room temperature.

3. Emission spectra have been photographed for several chelates at room temperature and at 77°K .

4. Data on lifetimes have been gathered from Professor Crosby and a few measurements have also been made using an apparatus constructed at STL.

5. A high-intensity, 10,000 joule, laser test apparatus, employing a confocal resonant cavity with multiple-layer dielectric mirrors, has been constructed. This apparatus can be used for evaluation of liquid laser materials, either in liquid solutions or in rigid glasses, and at any temperature from room temperature down to 77°K .

6. Selected chelates of europium, terbium and samarium have been tested in the above apparatus as a function of solvent, concentration, temperature and flash energy.

7. In rigid glassy solvents at 77°K no laser action has been observed. At the higher flash energies, bubble formation and photochemical decomposition with the formation of particles of carbon present problems.

8. In fluid solutions at low temperatures ($100 - 150^{\circ}\text{K}$) and high flash energies (8,500 joules), a few very recent experiments have yielded results which look like stimulated emission. However, without further experiments and demonstration of reproducibility, it is impossible to know whether these represent authentic laser action or not.

IV. Preparation of Materials

A. Rare-Earth Chelates

The dibenzoylmethide complexes (MD_3), the benzoylacetates (MB_3) and the acetylacetates (MA_3) were generously supplied to us by Professor G. A. Crosby. Some compounds were also purchased from Dr. R. E. Whan, 925 Truman, N.E. Albuquerque, New Mexico. Methods of preparation were as follows.

Acetylacetates

The rare earth oxide was dissolved in a concentrated solution of HCl in H_2O , and the excess HCl was removed by evaporation. A three- to five-fold molar excess of liquid acetylacetone was added to the nearly neutral solution of rare-earth chloride, and concentrated ammonium hydroxide was added drop by drop with stirring to precipitate the chelate. The precipitated material was washed with water, air dried, and recrystallized once from acetone.

Benzoylacetates and Dibenzoylmethides

A solution of the rare-earth chloride in ethanol was treated with a solution of the chelating agent in the same solvent. The precipitation was accomplished by addition of piperidine. The products were recrystallized from an appropriate solvent (methanol, ethanol or acetone) and either air dried or vacuum dried. The chelates were analysed for percent metal by combustion techniques.

Thienoyltrifluoroacetylacetates

The Eu and Tb compounds $M(TTA)_3$ of the above ligand were prepared at STL in the following manner,

(a) Via the Sodium Salt of the Ligand

The compound, 4,4,4-trifluoro - 1 - (2-thienyl) - 1,3-butanedione was obtained White Label grade from Eastman. It had an orange color and did not appear to be very pure. Twenty grams of the compound was recrystallized from

methylcyclohexane, air dried, then vacuum dried at room temperature, yielding 13 grams of white crystals mp = 44°C to 46°C .

The ligand, (22.5m moles), was refluxed in p-xylene with sodium (22.5m moles). The p-xylene had been previously dried by refluxing over sodium ribbon. After four hours only a few specks of sodium remained. On cooling, the reaction mixture yielded 2.6 gms of the sodium salt, NaTTA, as cream white crystals for a 48% yield based on the first crop without further work-up of the mother liquor.

To an aqueous solution containing 5m moles of NaTTA was added with stirring an aqueous solution of 1.66m moles of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The reaction mixture turned cream-colored and an oil precipitated. After chilling the mixture in ice, the oil was extracted with ether until no further fluorescence was present in successive extracts. Some difficulty was experienced in obtaining a crystalline product. On concentrating the solution there was a tendency for a gummy precipitate to form. However, by chilling and washing the precipitate several times with cyclohexane, in which the gummy material was somewhat insoluble, a solution was obtained which, after concentrating and cooling, yielded a pale brown precipitate. This was filtered off and recrystallized from cyclohexane. The yield was about 20%. This material tended to sublime between 108 and 140°C with very little true melting. On the above evidence it would not appear to be very pure. Nevertheless its solutions yield a very strong red fluorescence even at room temperatures and the absorption and emission spectra (Section V) appear to be those of a fairly pure compound.

(b) With the Aid of Piperidine

A different method was used for preparing the Terbium compound. To a solution of 2.45m mole of the ligand in 200ml of absolute ethanol was added an 8m mole excess of redistilled piperidine (Eastman White Label). Anhydrous TbCl_3 , prepared by

heating 0.15g of the oxide with ammonium chloride at 300°C, was dissolved in 400ml of absolute ethanol and added in 50ml increments to the piperidine solution. The reaction mixture was refrigerated overnight and then the volume was reduced to 100ml by distillation under reduced pressure. This reduced volume was chilled with tap water and the precipitate collected and washed with cold methanol. After air and vacuum drying it gave 0.35gm. of snow white crystals for a 52% yield of $\text{Tb}(\text{TTA})_3$.

Solutions of this material fail to fluoresce at room temperature but fluoresce green when cooled in liquid nitrogen.

B. Solvents and Low-Temperature Glasses

Various mixtures of organic solvents, when cooled to 77°K, set to a rigid glass. Such glasses have been extensively used in the past for studies of phosphorescence. Laser experiments at 77°K demand glassy media which must:

1. Be rigid, transparent and free of cracks, voids and other optical defects.
2. Have sufficient solvent power to hold the luminescent compounds in solution at 77°K.
3. Have high enough melting-point, thermal conductivity and specific heat not to melt on flashing.
4. Be free enough of mechanical strain to tolerate the presence of an embedded metal laser cavity without cracking.

Many solvent mixtures which form glasses at 77°K have been described in the literature (22). Common formulations are EPA (ether, isopentane and ethanol in the ratio 5:5:2 by volume) and 3MP (3-methyl pentane and iso pentane in 3:1 ratio).

The biggest problem in our experiments has been to satisfy the fourth requirement above. While good glasses can be made in an empty cell, introduction of the metal laser assembly leads to cracking and formation of voids. Detailed investigations finally laid the problem to three causes:

1. The upper mirror mount of the confocal cavity hinders the very considerable (20%) shrinkage of the solvent which occurs on cooling. This causes formation of a void under the top mirror.

Remedy: Widen the cell at this point to form a "spare-tire" as shown in Figure 23. This also provides a reservoir to make up for shrinkage.

2. The glass may set and become rigid too far above 77°K . Further cooling causes further shrinkage which sets up strains and leads to cracking.

Remedy: Choose a solvent mixture which retains enough plasticity to relieve strains down to temperatures not much above 77°K .

3. Presence of small amounts of dissolved water which tend to crystallize at 77°K and precipitate cracking.

Remedy: Thorough drying of all solvents by refluxing over metallic sodium (or sodium ethoxide for alcohol) followed by distillation through a good column.

Solvents are then stored over sodium ribbon or sodium ethoxide in sealed flasks vented via a drying tube to prevent ingress of atmospheric moisture.

In addition to containing dissolved water, many so-called "high-purity", Spectrograde and Research Grade solvents were found to possess impurities which give a bluish phosphorescence of long duration (several seconds) at 77°K . Although for many experiments this phosphorescence was too weak to interfere with observations, it was deemed desirable to get rid of it. Spectrophotometric analysis reveals absorption bands in the region 256 to $270\text{ m}\mu$. Coupled with the long-lived blue phosphorescence, this suggests that the most likely impurity is benzene. As shown in Figure 5, the unwanted absorption can be removed, for the hydrocarbon solvents, by chromatographic purification using a column of 3-X molecular sieve. Distillation and fractionation ~~and fractionation~~ columns have now been set up for purification of ethanol, butanol, ethyl ether, 2-methyl butane and 3-methyl pentane in quantities of several liters at a time.

Using anhydrous, purified solvents, a large number of glasses have been formulated of which several meet the requirements outlined earlier. The most generally useful are:

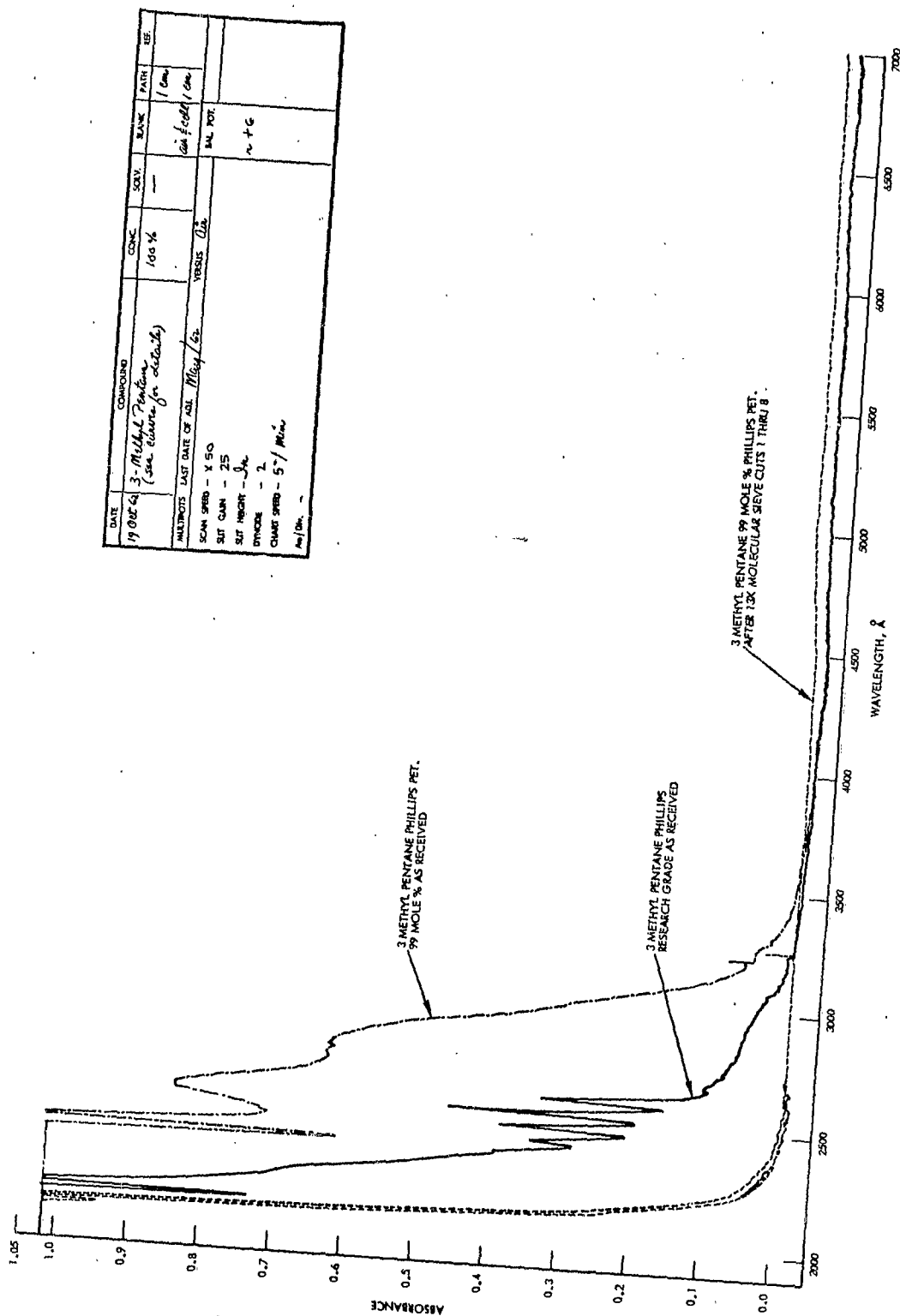


Figure 5. Spectral Absorption of Hydrocarbon Solvents Before and After Purification

DATE	COMPOUND	CONC.	SOLV.	BLANK	PATH.	REF.
19 Oct 64	3-Methyl Pentane (see above for details)	100 %	—	air feed / cm	1 cm	
ANALYSTS	LAST DATE OF AIL May 62	VERBIS Q12				
SCAN SPEED - Y 50						
SIT GAIN - 25						
SIT HEIGHT - 50						
SYNCHRO - 2						
CHARGE SPEED - 57 / Min						
Re / Min						
				n + 6		

(a) 3-methylpentane and 2-methylbutane (iso pentane)
(3:1 by volume).

(b) 2-methylbutane and n-butanol (7:1 by volume).

Mixture (a) dissolves aromatic hydrocarbons and their derivatives and has been used for laser studies with benzophenone. Mixture (b) is more polar in nature and dissolves rare-earth chelates. Two other useful mixtures, are,

(c) 3-methylpentane:isopentane:ether:ethanol
(6:2:5:1 by volume).

(d) Isopentane:n-propanol (3:1 by volume)

Finally, it has been discovered that some solvents which normally fail to give a good glass at 77°K , will do so if the solvent is first degassed. Two examples are pure isopentane and pure USP grade mineral oil.

A list of glass compositions which can be used in the presence of embedded metal parts is given in Table III. In Table IV there is given a list of additional glasses which may be used for low temperature optical experiments when no metal parts are present.

As the experimental laser program progressed, it became apparent that even the best glasses showed unrelieved strains at 77°K , as revealed by examination under polarized light. Such strains spoil the optical quality of the medium, lead to deviation and attenuation of a light beam and could thus prevent the appearance of oscillations in the cavity. With this in mind and since several of the chelates have fairly good quantum yields even in liquid solutions, it was decided to carry out some experiments with low-temperature liquid solutions. Several of the mixtures previously used as glasses at 77°K were found to remain liquid down to quite low temperatures on addition of propane. Since propane is a gas at room temperatures

Table IIIGLASSES COMPATIBLE WITH EMBEDDED METAL PARTS

Components	Abbrevia- tion	Ratio by Volume	Solubility for Chelates
3-methylpentane		pure	ca. 10^{-4} M
Isopentane(2-methylbutane)		pure	ca. 10^{-4} M
3-methylpentane:isopentane	3MP:IP	3:1	ca. 10^{-4} M
Isopentane:isopropanol	IP	3:1	ca. 10^{-3} M
Isopentane:n-butanol	IB	7:1-7:3	ca. 10^{-3} M
3-methylpentane:isopentane: ether:ethanol	3MPIEE	6:1:5:1 6:2:5:1 6:4:5:1 4:4:5:1 7:2:5:1	ca. 10^{-3} M

Table IV

OTHER USEFUL 77°K GLASSES FOR OPTICAL WORK

Components	Ratio by Volume
Isopentane:methylcyclohexane	5:1
Isopentane:3-methylpentane:methylcyclohexane	6:2:2
Isopentane:3-methylpentane	9:1
Isopentane:n-propanol:methylcyclohexane	3:1:1: to 8:1:1
Isopentane:isopropylether	9:1
Isopentane:n-propanol	7:1 and 1:1
3-methylpentane:n-propanol	7:1 and 1:1

(boiling point -42°C), the following procedure was used. The chelate was first dissolved in the solvent in which it had the highest solubility e.g. butanol. Then the other liquid components were added and the mixture cooled in liquid nitrogen. Finally propane was bubbled into the cold solution, where it condensed to a liquid until the required volume was reached. Table V gives a list of mixtures useful for low-temperature liquid laser experiments.

C. Plastic Media

The preparation of plastic rods containing benzophenone and other aromatic compounds and some preliminary laser experiments with these rods were described in the Semi-Annual Report (23). Attempts to incorporate rare-earth chelates into polymethylmethacrylate have not been very successful, probably because of chemical reaction during the long curing period (7 days). A small amount of effort has been devoted to preparing specimens of epoxy resins containing europium benzoylacetonate and other chelates. While some of these yielded the characteristic red europium fluorescence at room temperature, the material possessed a yellowish color and did not appear to be favorable for laser experiments. Consequently, it was decided to drop further experimentation with plastics and to devote our efforts more directly to the search for liquid laser materials.

Table V

LIQUID MIXTURES FOR LOW-TEMPERATURE LASER STUDIES

Components	Ratio by Volume	Approx. temp. at which mixture attains "molasses" viscosity
Isopentane:butanol:propane	2:1:2	ca. 100°K
Isopentane:butanol:propane	6:1:5	77°K
Isopentane:butanol	7:1	ca. 128°K
Isopentane:3-methylbutane	1:1	ca. 128°K
95% Ethanol:n-propanol	1:1	163°K
95% Ethanol:methanol	1:1:1	163°K
95% Ethanol:n-propanol:methanol	1:1	153°K
Methanol:n-propanol	1:1	148°K

V. Spectroscopic Studies

A. Absorption Spectra

The absorption spectra of chelates investigated for laser properties were recorded using a Cary model 14 spectrophotometer. Most chelates were studied in solution at concentrations of about 10^{-5} M in various solvents of interest. All absorption spectra were recorded in the presence of air.

Figures 6,7 and 8 are reproductions of Cary traces of typical spectra. Traces are obtained in units of optical density (i.e., $\log I_0/I_t$ where I_0 is the unattenuated light intensity and I_t is the beam intensity after it has traversed the absorbing medium). Traces can be converted from optical density to extinction coefficient by use of Beer's Law:

$$\log_{10} I_0/I_t = \epsilon cl$$

where ϵ is the extinction coefficient, c the concentration and l the pathlength. The wavelength of maximum absorption and extinction coefficient at this wavelength are given below for several chelates.

Chelate	EuB ₃	Eu(TTA) ₃	TbA ₃
λ_{\max} (Å)	3200	3410	2750
ϵ_{\max}	36,000	36,800	25,000

Since the absorption spectrum of a chelate is determined mainly by the ligand, these traces are typical of all chelates containing the same ligand with different rare earth ions.

Traces were taken with fresh samples only. Dilute solutions (10^{-5} M and lower) of rare earth chelates exposed to air tend to decompose a short time after they are prepared, possibly because of dissociation. Concentrated solutions are usually much more stable but they too decompose with time (several days). The

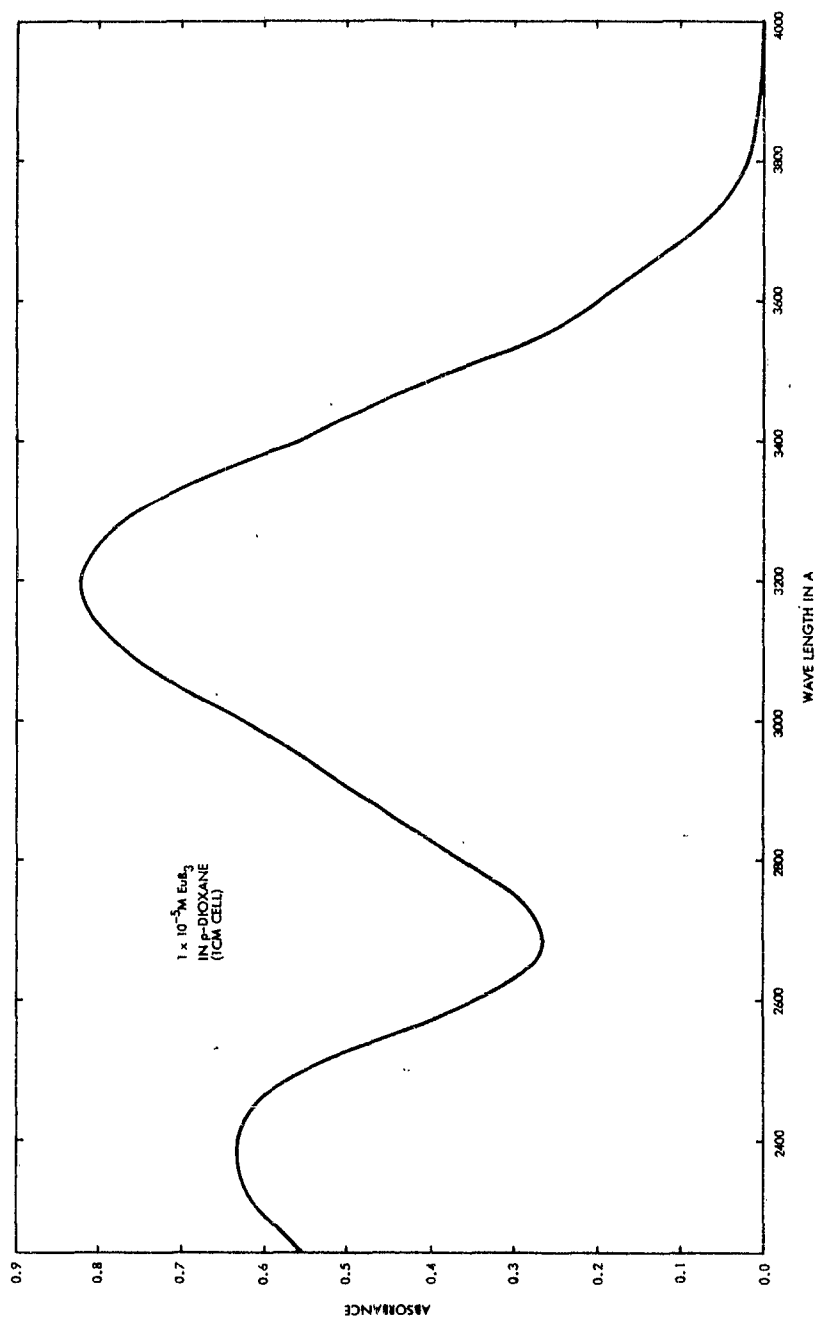


Figure 6. Absorption Spectrum of EuB_3

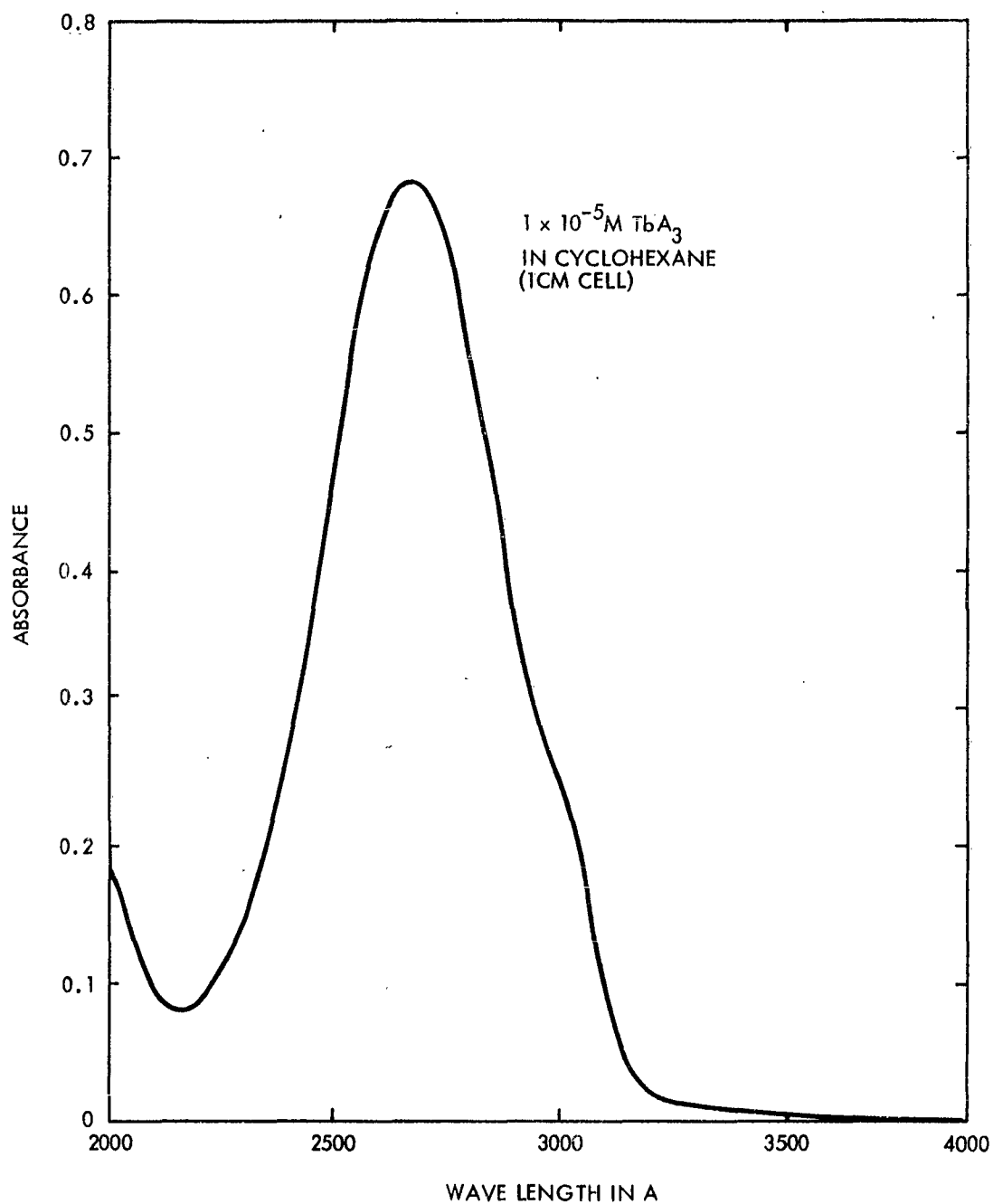


Figure 7. Absorption Spectrum
of TbA_3

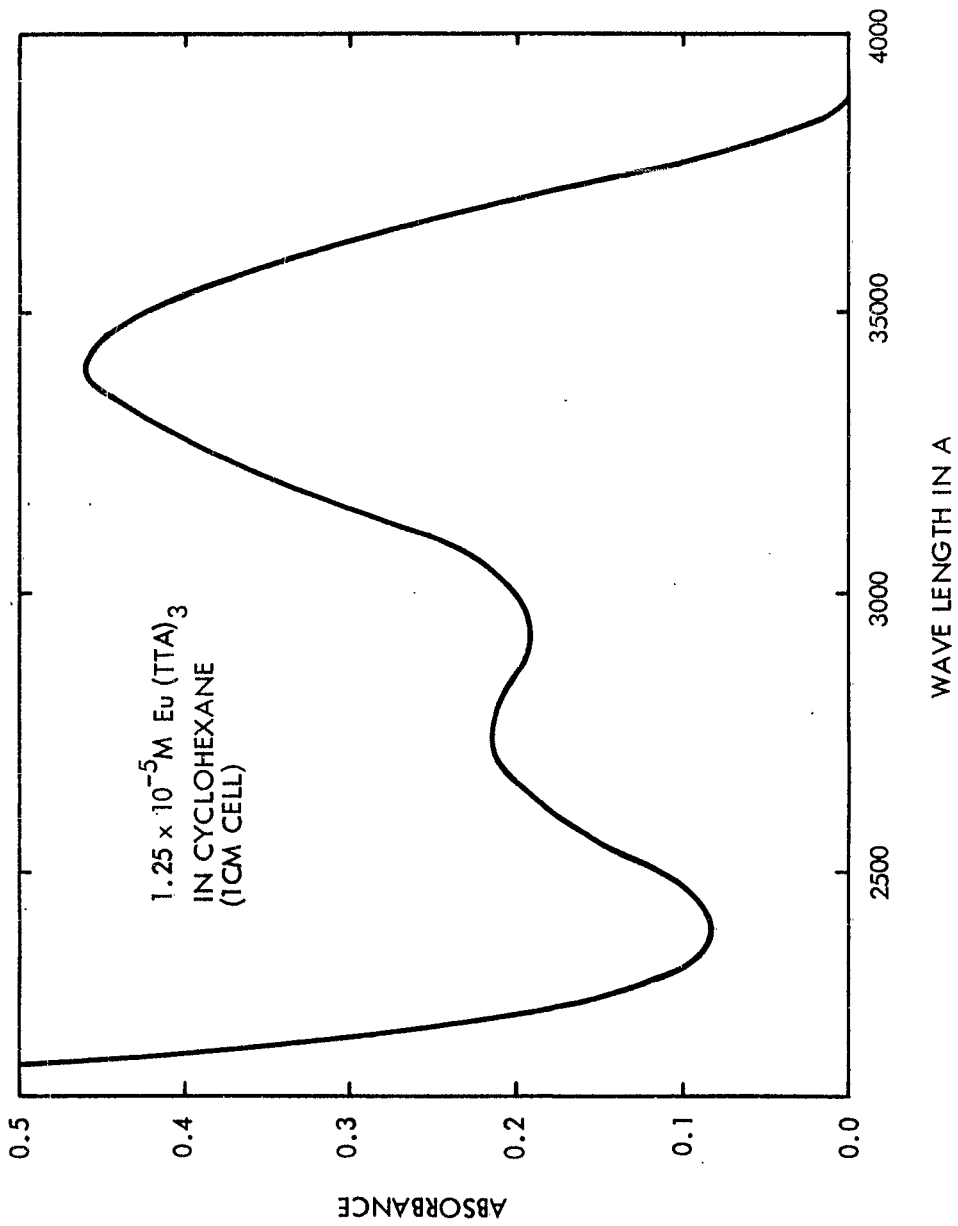


Figure 8. Absorption Spectrum of Eu(TTA)₃

absorption spectrum of a chelate will decrease in time in an irreversible manner corresponding to this decomposition of chelate. This effect is particularly noticeable in alcoholic or ether solutions but also occurs, though more slowly, in hydrocarbon solvents. Apparently oxygen interaction is also, in part, responsible for this decomposition. We did not undertake an intensive investigation of this phenomenon and have made no effort to interpret the effect. The effect is significant in future considerations of a specific chelate system as potential laser material since stability will be important in this regard.

B. Emission Spectra

Fluorescence spectra for several terbium and europium chelates were recorded on a Jarrell-Ash Model 75-000 spectrograph. (Figure 9). Some typical spectra are shown in Figures 10, 11 and 12 . The spectra in rigid glasses at liquid nitrogen temperatures were bright enough to be recorded in a few minutes at a narrow slit opening.

Figure 10 shows the emission spectrum of TbA_3 in a glass of 7 parts isopentane and 1 part butanol at liquid nitrogen temperature. The bright band extends from $18,100$ to $18,500\text{cm}^{-1}$. The single bright line occurs at about $18,400\text{cm}^{-1}$ and is approximately 20Å wide. The other side bands are much weaker and are only detectable at very long exposure times.

The emission spectrum of $Eu(TTA)_3$ at $5 \times 10^{-5}\text{M}$ in a 7:1 glass (see above) at liquid nitrogen temperatures is shown in Figure 11. The main emission band occurs between $16,520$ and $16,100\text{cm}^{-1}$. The bright line emission in this band occurs in a band 10Å wide at $16,290\text{cm}^{-1}$.

The narrow bands observed at liquid nitrogen became quite broad at room temperature. The emission of $Eu(TTA)_3$ at room temperature (upper two spectra) is compared to that at liquid nitrogen temperature (lower three spectra) in Figure 12 .

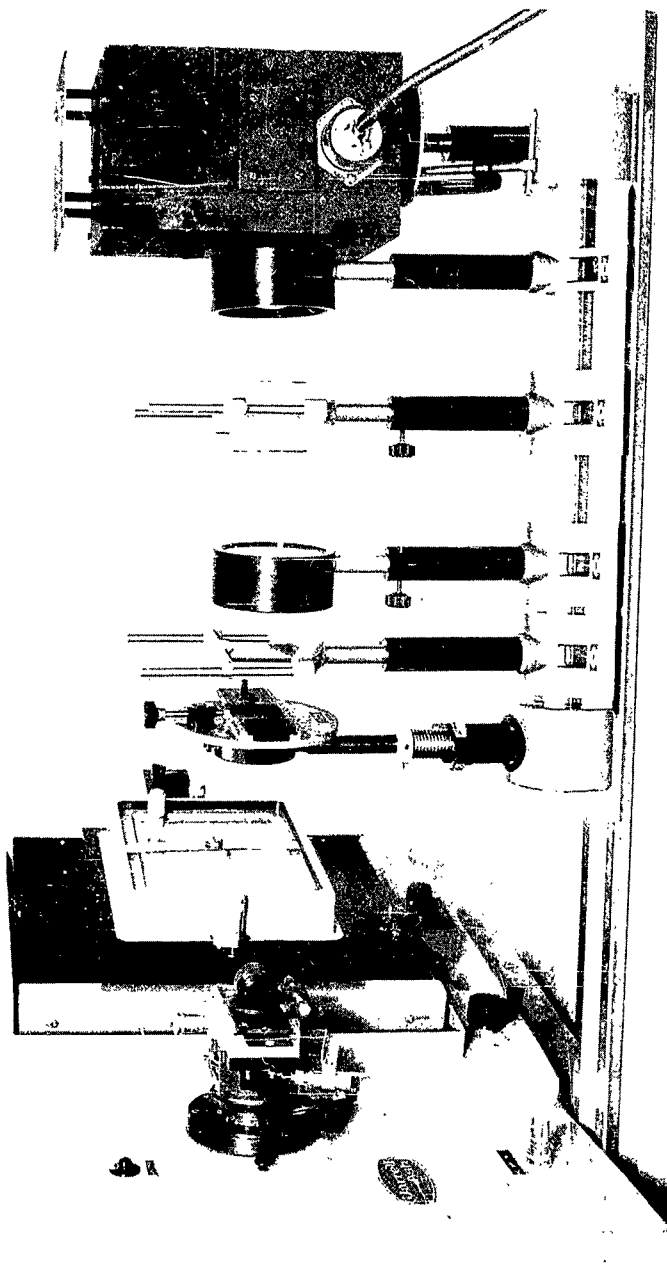


Figure 9. Jarrell-Ash High Aperture Grating Spectrograph

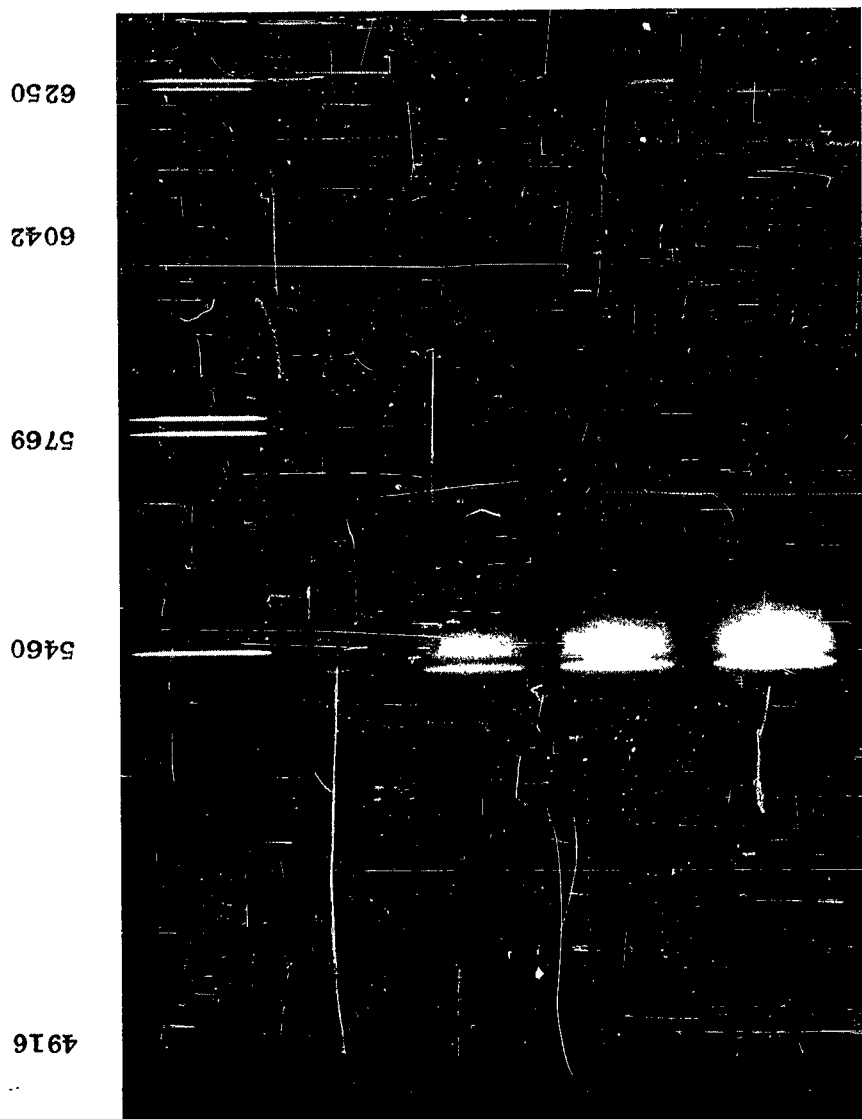


Figure 10. Emission of TbA_3 in IPB Organic Glass at $77^\circ K$
(Mercury reference spectrum in A)

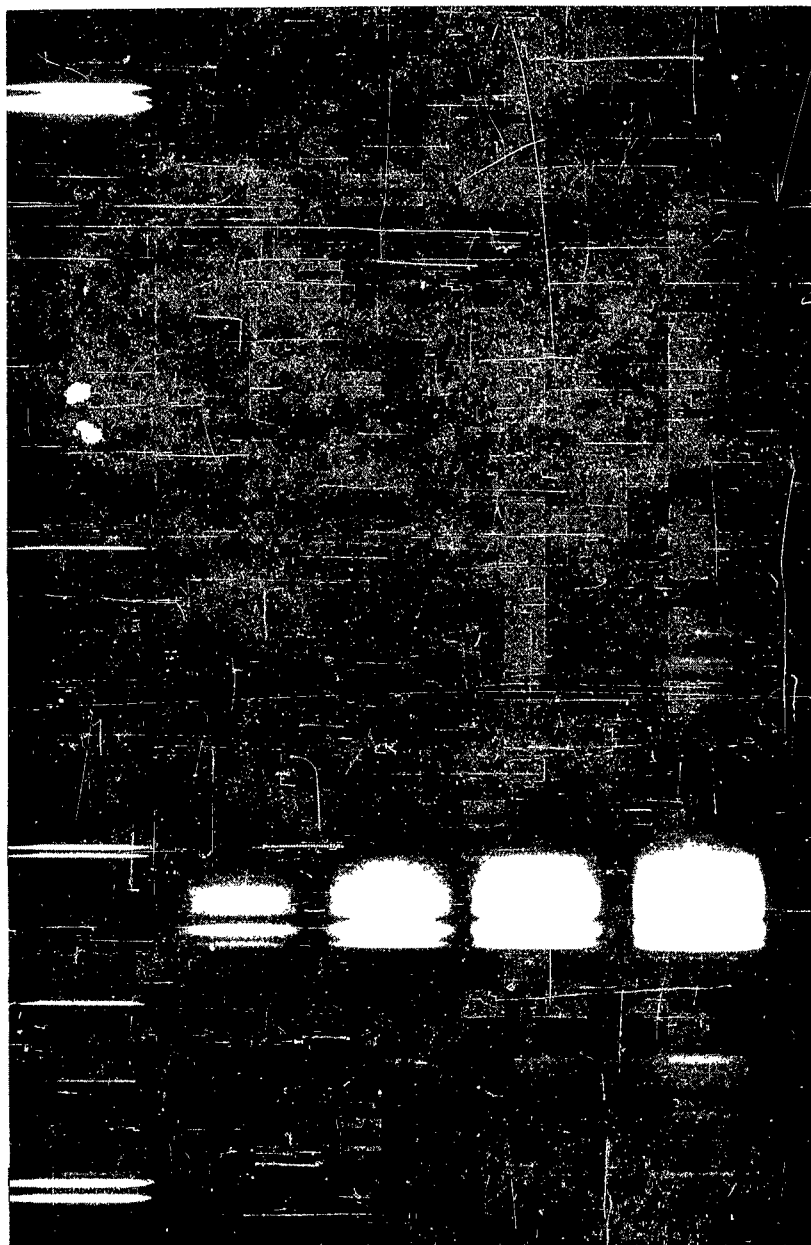


Figure 11. Emission of $\text{Eu}(\text{TFA})_3$ in IPB Organic Glass at 77°K
(Mercury reference spectrum in A)

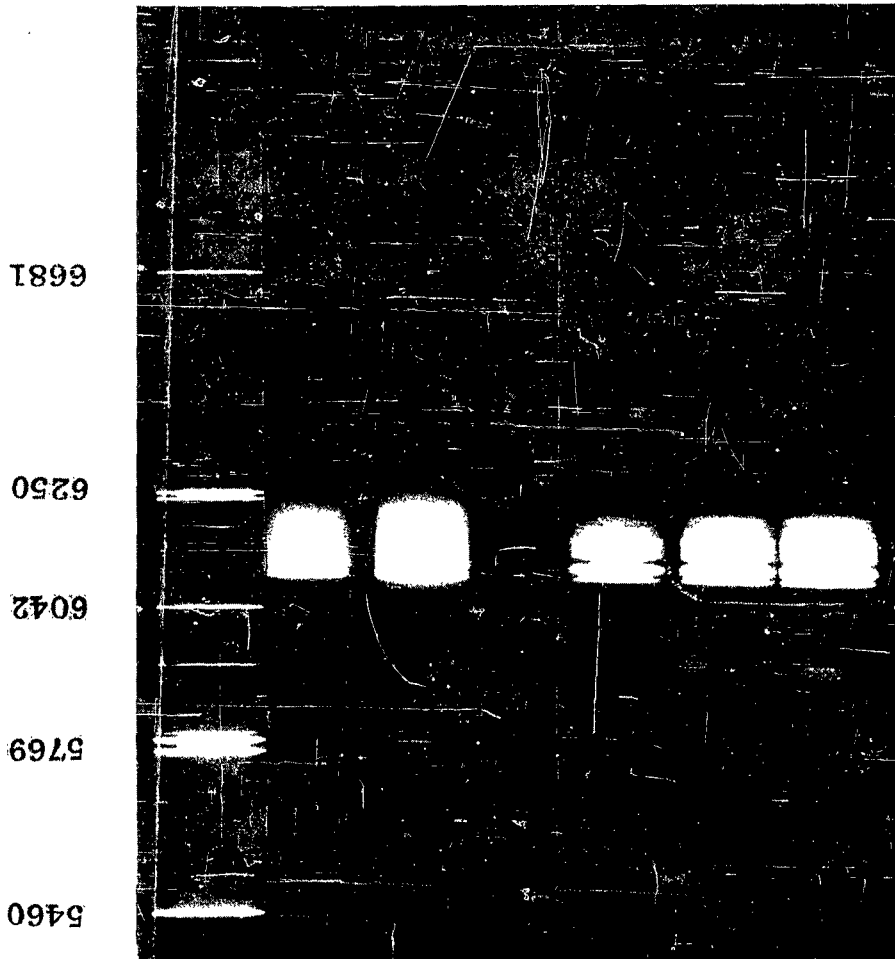


Figure 12. Emission of $\text{Eu}(\text{TTA})_3$; upper two spectra in IPB solution at room temperature; lower three spectra in IPB glass at 77°K . (Mercury reference spectrum in A)

The exposure times and slit widths of both exposures at room temperatures are the same as for the lower two exposures at liquid nitrogen temperatures. It is evident that structure in the emission bands, present at liquid nitrogen temperature is absent at room temperature.

Figure 13 gives the room temperature emission of $\text{Eu}(\text{TTA})_3$ in tetrahydrofuran recorded photoelectrically through a monochromator. It is seen that the single sharp line is no longer present but that the main emission consists of a band from $16,450$ to $15,900\text{cm}^{-1}$ with a maximum at $16,300\text{cm}^{-1}$. The total band is shifted slightly to the red but the peak occurs at the same energy. Figure 13 also shows a photoelectric trace of TbA_3 emission in cyclohexane at room temperature. Here some band structure is preserved in the main band. The emission occurs between $18,660\text{cm}^{-1}$ to $17,850\text{cm}^{-1}$ with a maximum at $18,250\text{cm}^{-1}$. The main band is approximately 50\AA wide. There appears to be considerable shifting of levels from those observed at liquid nitrogen temperatures. We have not attempted a complete analysis of the emission spectra of these chelates.

Despite the relative broadening at room temperature compared to 77°K , the lines are still fairly narrow even at room temperature. We have photographed the emission spectra only at liquid nitrogen temperatures and at room temperature. However, it is reasonable to assume that there is a continuous narrowing of the lines as the temperature is lowered from room temperature to liquid nitrogen temperature. This implies a continuous decrease in the threshold for laser action as the temperature is decreased.

Preliminary measurements indicate that the emission of the same chelate in different solvents varies but little from solvent to solvent. There are slight but definite variations in the emission spectra of chelates in which the ligand is varied while the rare earth ion remains the same. Thus it may be possible to find a ligand with high yield that optimizes the narrow line emission even up to room temperature.

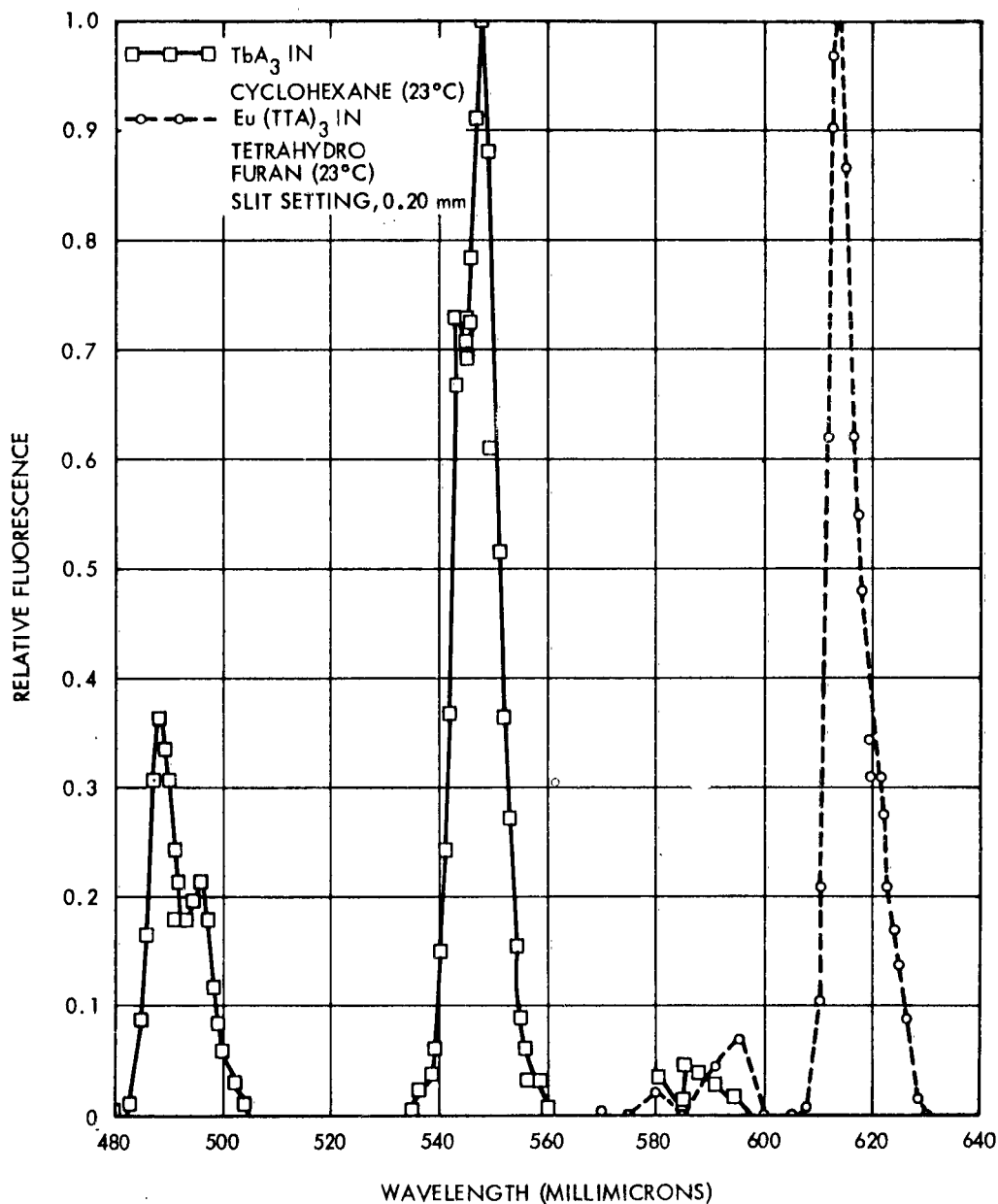


Figure 13. Emission Spectra of TbA_3 and $\text{Eu}(\text{TTA})_3$

The important role played by the ligand is shown by the fact that, whereas TbA_3 solutions show strong fluorescence at room temperature, TbB_3 gives little or no emission unless the solution is cooled. For europium, on the other hand the reverse is true; EuA_3 gives hardly any emission at room temperature whereas EuB_3 is quite bright and Eu(TTA)_3 emits very strongly indeed.

VI. Quantum Yield and Lifetime Measurements

A. Measurement of Quantum Yields

1. Background

The quantum yield of fluorescence of a molecule is the probability that the molecule will radiate a photon after absorbing a photon. The quantum yield may also be regarded as the lower limit of the probability of populating the upper excited state, which is associated with the fluorescent transition, on absorption of a photon. Radiationless deactivation of the upper excited state would raise the probability of populating the excited state above the ^{measured} quantum yield. Quantum yield measurements may therefore be employed as one index of the practicability of obtaining a high enough concentration of molecules in an upper level to achieve laser action. Consequently instrumentation was constructed for measurement of quantum yields (Figures 14, 15 and 16).

A literature survey indicated that two practicable methods of measuring absolute quantum yields had been developed; one by Weber and Teale (24) and the other principally by Bowen and Melhuish (25,26). The Weber-Teale (WT) method initially seemed to be the more accurate of the two methods; therefore an instrument was built at STL to make quantum yield measurements by the WT technique. Concentrations of fluorescent material in a laser would generally be above the concentrations used in the WT technique and below the concentrations used in the BM technique. The optical density per centimeter of the fluorescent material to the exciting light is typically 2 to 4 in the BM measurements, 0.001 to 0.10 in the WT measurements, and approximately 1 in a typical laser. Therefore, the instrument was modified so that quantum yields could be determined by both techniques, to afford measurement capability over increased concentration ranges bracketing probable concentrations which would be used in a laser. Furthermore the quantum yields of some fluorescent materials often

cannot be determined effectively by one or the other method. Sometimes fluorescent compounds are not soluble enough in a solvent to be effectively tested by the BM method, while other fluorescent compounds e.g., the chelates, tend to dissociate or rapidly deteriorate at the low concentrations used in the WT method. The instrument developed at STL for making quantum yield measurements is described in the following sections along with procedures for measuring quantum yields by both the WT and the BM technique.

An instrument is also described which was constructed to provide the capability of making relative fluorescent intensity measurements as a function of temperature. Measurements of the relative fluorescent intensities from a molecule at low temperatures and room temperature have been combined with values of quantum yield at room temperature to give estimated quantum yields at the low temperatures. Relative fluorescent intensity measurements can be made relatively quickly, which makes them useful in determining decreases of fluorescence with increasing solution age and in selecting a solvent to maximize quantum yields.

2. Quantum Yield Measurements by the Weber-Teale Technique

The configuration of the instrument, adapted to making quantum yield measurements by the WT technique (Figure 16) includes a high pressure mercury lamp, lens and filters that afford reasonably monochromatic (315 or 365m μ), collimated, excitation light, which is subsequently passed through an absorption cell. Fluorescence, which is emitted perpendicular to the excitation beam and the plane side of the absorption cell is detected with an RCA 6217 photomultiplier tube. The quantum yield of fluorescence is estimated, by comparing the photomultiplier currents when the cell is filled with either a fluorescent solution or a light scattering solution (colloidal silica, "Ludox L.S.") having an equal optical density at the wavelength of the excitation light. The excitation

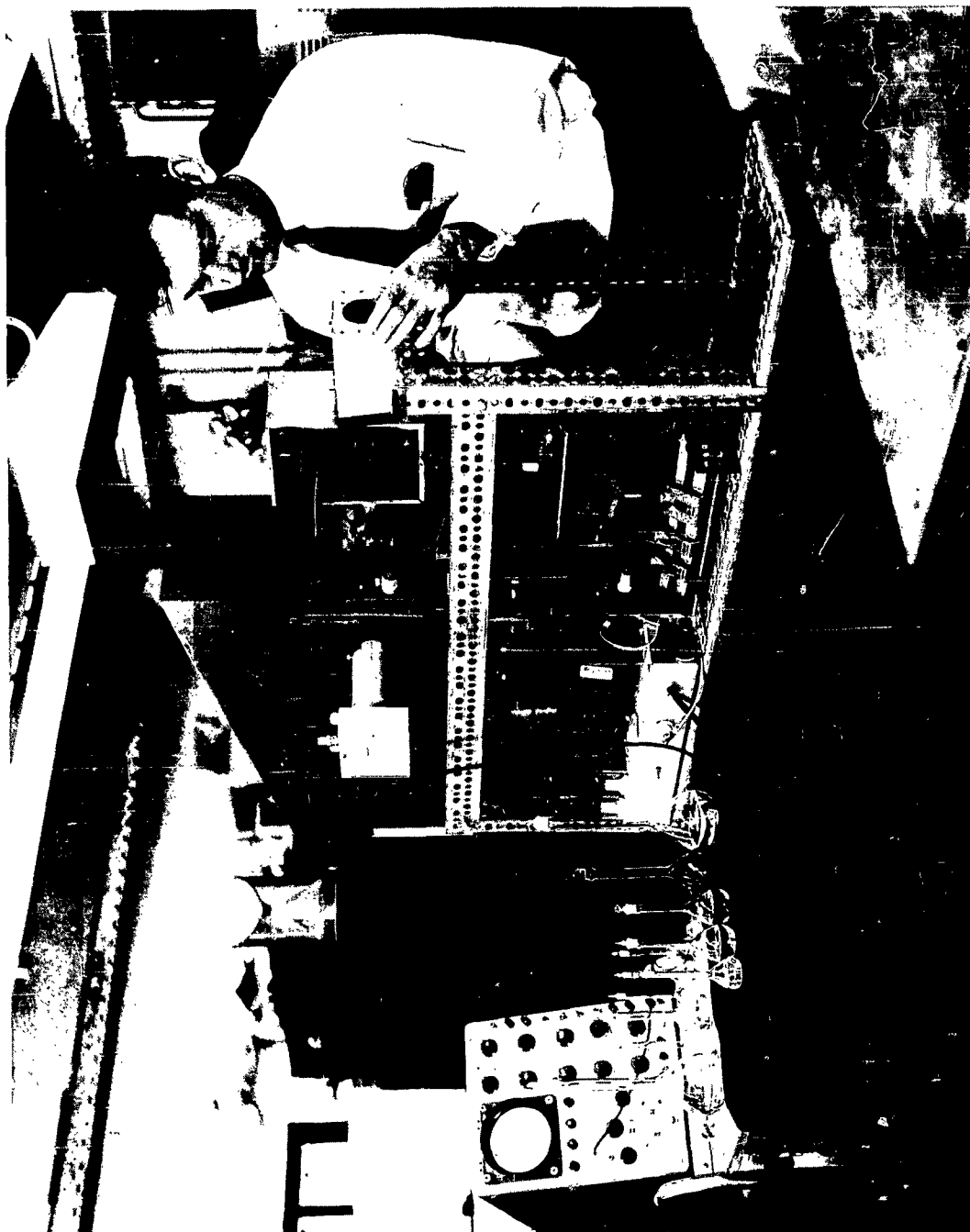


Figure 14. Quantum Yield Apparatus

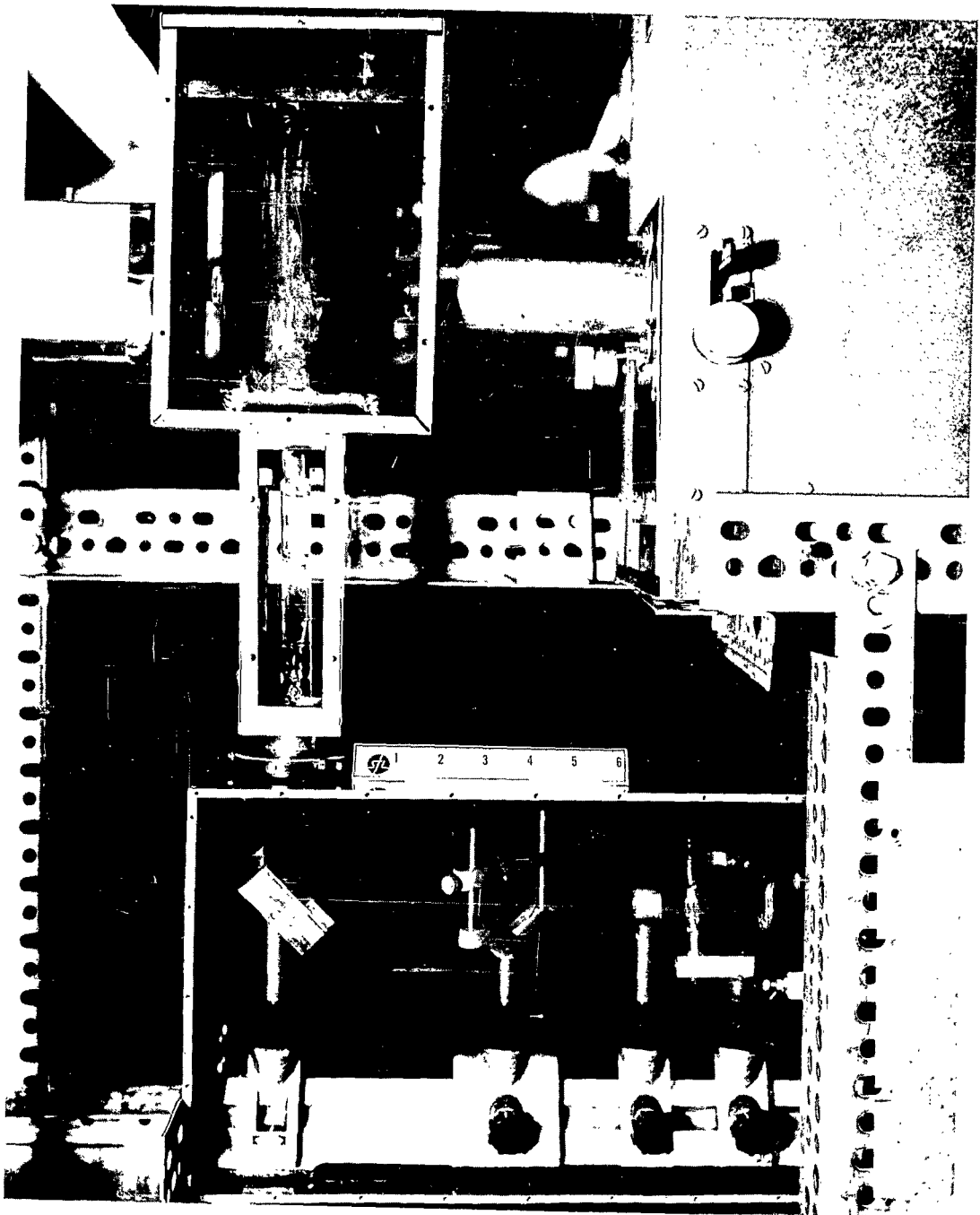


Figure 15. Close-up of Quantum Yield Apparatus showing Optics and Sample Cell

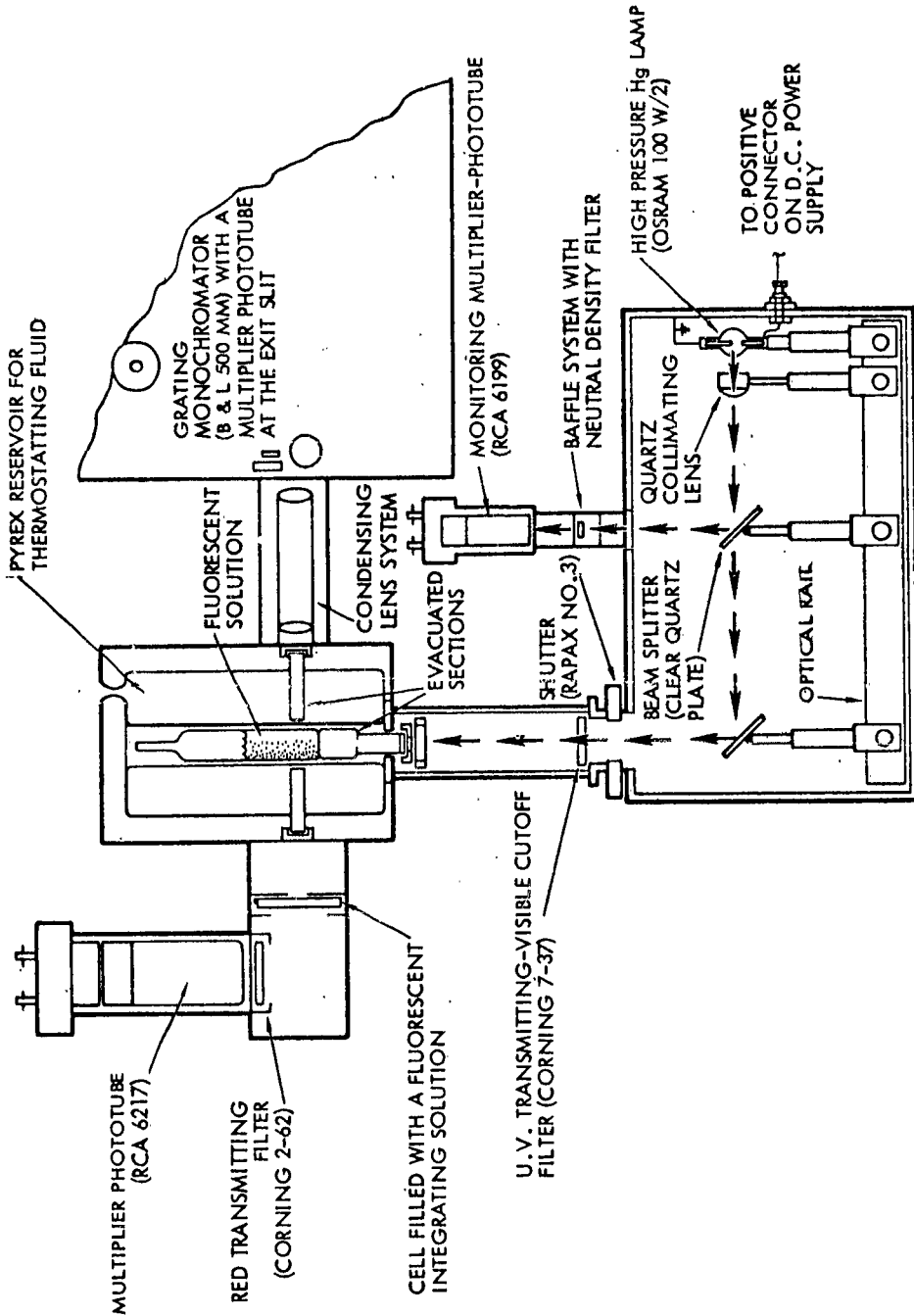


Figure 16. Schematic Diagram of Quantum Yield Apparatus

light is attenuated exponentially and equally, in the one case by absorption and in the other by scattering, with the distance of penetration into respectively the fluorescent and the light scattering solutions. This makes the geometry of transverse light emission similar in the two cases. Furthermore, photons are not lost by absorption in the light scattering solution, so that attenuated light is scattered quantitatively from the cell to give an approximation of the photon flux from a fluorescent solution having a quantum yield of one. The quantum yield is determined in practice, however, from the ratio of the slope of the photocurrent-optical density plot for the fluorescent solution to the corresponding slope for the light scattering solution (Figure 17). This ratio is equivalent to the ratio of the photocurrent produced by a fluorescent solution to the photocurrent produced by a scattering solution of equal optical density to the excitation light. Weber and Teale have indicated that the ratio of photocurrent-optical density slopes must be multiplied by two other factors to give the true quantum yield.

$$\phi = \left(\frac{\left[\frac{dF}{dE_{\lambda_0}} \right]_{E_{\lambda_0} \rightarrow 0}}{\left[\frac{dS}{dE_{\lambda_0}} \right]_{E_{\lambda_0} \rightarrow 0}} \right) \cdot \left(\frac{3 + P_f}{3 + P_s} \right) \cdot \left(\frac{f_{\lambda_0}}{f_{\lambda_f}} \right) \cdot \left(\frac{n_f}{n_s} \right)^2 \quad -5.1$$

where, ϕ is the quantum yield.

The first factor ~~in brackets~~ is the ratio of slopes of the photocurrent-optical density plots of luminescent and scattering solutions. F and S are the photocurrents from the fluorescent and scattering solutions respectively. E is the optical density and λ_0 is the wavelength of the exciting light. The subscript $E_{\lambda_0} \rightarrow 0$ indicates that the slopes should be taken,

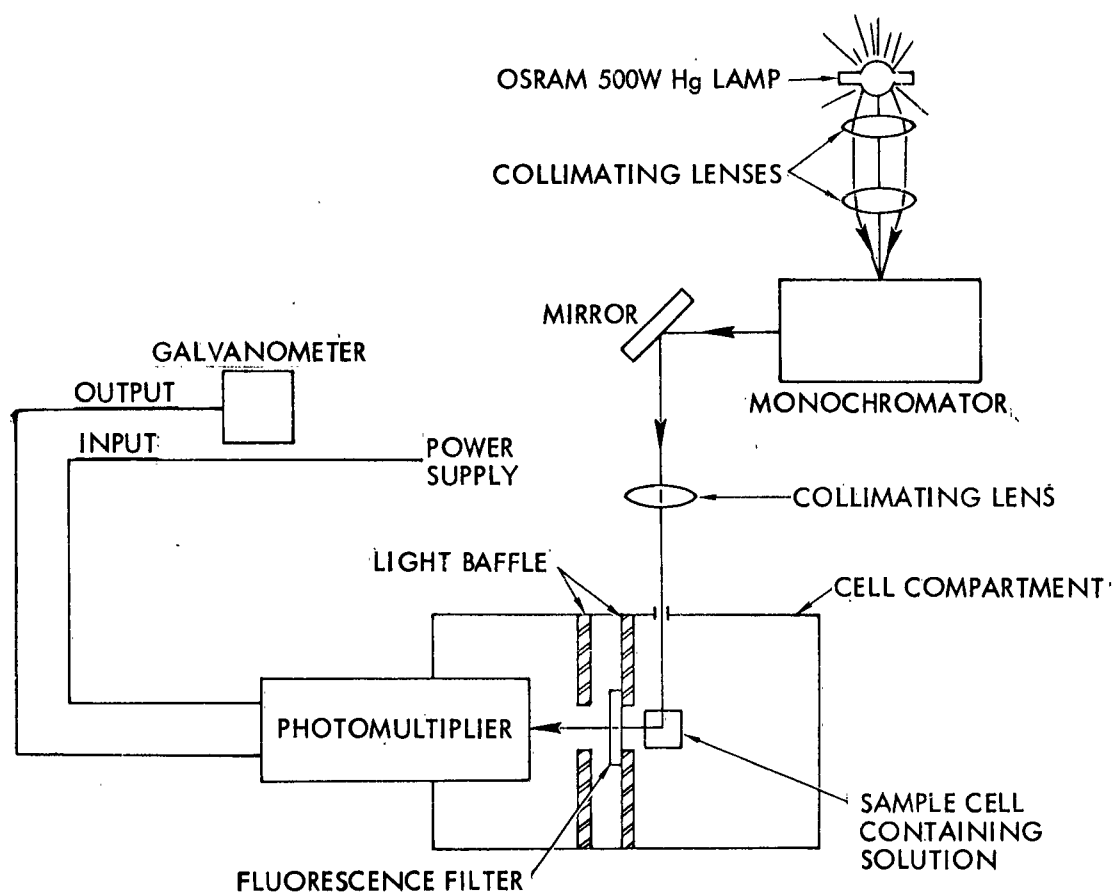


Figure 17. Typical Plots for Quantum Yield Determination

as nearly as is possible, at zero optical density.

The second bracketed factor $\left(\frac{3 + P_f}{3 + P_s} \right)$ corrects

for deviation from equal intensity of scattered or fluorescent light as a function of direction. This is characterized by polarization of the light emitted perpendicular to the direction of the excitation light. P_f and P_s are the polarizations of the transversely emitted fluorescent and scattered light respectively. P_s is nearly one and P_f is nearly zero for fluorescence from fluid solutions, which makes $\left(\frac{3 + P_f}{3 + P_s} \right)$ nearly equal to 0.75 for all the

systems which have been investigated up to the present time. The zero value of P_f indicates that the fluorescence is spherically symmetrical, while the value of one for P_s indicates that the light scattered parallel and antiparallel to the direction of the excitation light is twice as intense as light scattered normal to the direction of the excitation light. As a result, compared to the fluorescence, only three-quarters of the average intensity of the scattered light is detected, which makes the correction factor of three-quarters necessary.

The factor $\left(\frac{f_{\lambda_o}}{\overline{f_{\lambda_f}}} \right)$ in equation 1, is the ratio of the

photomultiplier current per incident photon of exciting light, f_{λ_o} , to the average photocurrent per incident photon of fluorescent light, $\overline{f_{\lambda_f}}$. It is necessary because the response of the photomultiplier tube varies with wavelength. It is possible to make f_{λ_o} equal to one by interposing a cell filled with rhodamine B between the photomultiplier tube and the scattering or fluorescent solution. The photomultiplier tube is arranged so that it views only the fluorescence of rhodamine B resulting from

absorption of the scattered or primary fluorescent light. Since the fluorescence yield of rhodamine B is independent of the wavelength of excitation over a wide range, the combination acts as a quantum counter, i.e., its response depends only upon the number of photons regardless of their wavelength.

Rhodamine B becomes transparent and is not useful at wavelengths longer than 600mμ. Beyond this wavelength, therefore, it is necessary to use the photomultiplier on its own and correct for the variation of its response with wavelength. The value of

$\frac{f_{\lambda_0}}{f_{\lambda_f}}$ can be calculated from a photomultiplier wavelength-

sensitivity curve. This is determined by comparing the response of the photomultiplier tube to that of a thermopile for identical fluxes of monochromatic light of various wavelengths. The response of the thermopile is closely proportional to the power of the incident light, which is in turn proportional to the photon flux divided by the wavelength of the light.

The factor $\left(\frac{n_f}{n_s}\right)^2$ in equation 1, where n_f and n_s

are the indices of refraction of the fluorescent and scattering solutions respectively, is not included in Weber and Teale's calculations, but is clearly necessary where the luminescent light is emitted nearly normally through planar windows to air(26).

$\left(\frac{n_f}{n_s}\right)^2$ compensates for the greater dispersion of light by diffraction in passing from the solution with the higher index of refraction to air.

Some difficulty was experienced in obtaining accurate results with the Ludox scattering solutions. The optical densities of these colloidal silica solutions were proportional to the inverse fourth power of the wavelength of the incident

light, which indicated that the attenuation of the incident light was caused solely by Rayleigh scattering with no significant absorption of light occurring. However, the optical density is not halved by halving the concentration of the Ludox solutions and for diluted solutions, slowly increases for weeks after dilution. This makes it necessary to check frequently on the optical densities of the Ludox solutions. These effects are probably caused by continuous dissociation of metastable clusters of silica particles which are too large to give Rayleigh scattering. Another problem encountered with Ludox solutions and strongly fluorescent solutions was that scattered fluorescent light reaching the detector of the Cary Spectrophotometer tended to indicate erroneously low values of optical density. This error was satisfactorily minimized by using a short absorption cell (2cm long), located as far from the detector of the Cary Spectrophotometer as was possible.

3. Quantum Yield Measurement by the Bowen-Melhuish Technique

In the BM method of determining quantum yields, a cell containing a concentrated solution of a fluorescent solution is illuminated by the monochromatic (315 or 365m μ) excitation beam, which is used in the WT configuration. The concentration of the solution is preferably large enough so that the excitation beam is largely absorbed in the first few millimeters of solution. The excitation beam is inclined at an angle of 45^o to the normal to the cell face. A RCA 6217 photomultiplier tube is placed on the same side of the cell face as the excitation beam and on the line which is normal to the cell face and intersects the 5mm diameter fluorescent spot created by the excitation beam. The geometry of the system and the intensity of the exciting light may be taken into account by measuring the signal from a diffuse reflector of magnesia or a solution of known quantum yield as a standard. Acid solutions of quinine sulfate have been proposed as a standard having a quantum yield of 0.55, (27) which is not subject to the complications of oxygen quenching or self absorption

of fluorescence. The quantum yield is then given by the expression

$$\phi_u = 0.55 \left(\frac{F_u}{F_q} \right) \cdot \left(\frac{n_u}{n_q} \right)^2 \cdot \left(\frac{\overline{f}_{\lambda_q}}{\overline{f}_{\lambda_u}} \right) \quad 5-2$$

where; ϕ is the Quantum yield of compound u. 0.55 is the quantum yield of quinine sulfate, F_u and F_q are photomultiplier responses and n_u and n_q are the indices of refraction for a solution containing respectively compound u and quinine sulfate. \overline{f}_{λ_q} and \overline{f}_{λ_u} are the average photomultiplier currents per incident photon of fluorescence from solutions of quinine sulfate and compound u respectively.

4. Relative Intensity Measurements

The intensity of fluorescence of an emitting species in a given environment is proportional to its quantum yield in that environment. The relative intensities of fluorescence of a rare earth chelate, in various solvents or at various temperatures, are a measure of the relative quantum yields, insofar as the emission characteristics of the chelate (e.g., spectral distribution of fluorescence) do not change as a function of environment. To a first approximation, we can assume that the spectral distribution of rare earth ion emission is independent of temperature and solvent. Then the ratio of the fluorescence intensities at any two temperatures will be equal to the ratio of quantum yields at these temperatures. Thus, provided the absolute quantum yield is accurately measured in a given solvent at one temperature, quantum yields at other temperatures and in other solvents may be obtained simply by taking fluorescence intensity ratios.

The experimental arrangement is shown in Figure 13. Light from an Osram 500 watt high pressure mercury lamp is passed through a Bausch and Lomb 250mm grating monochromator. The monochromatic beam is reflected at right angles from an aluminum

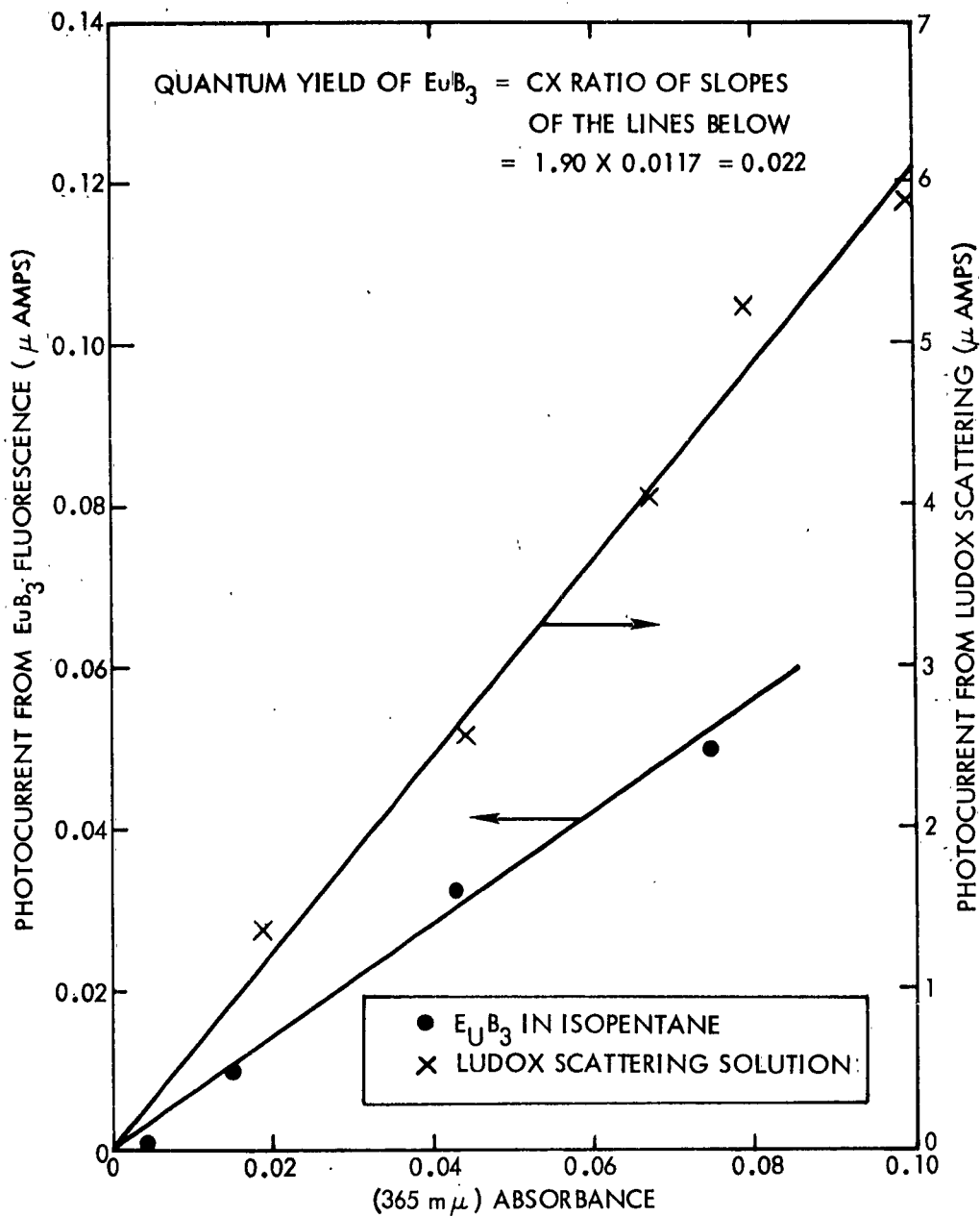


Figure 18. Apparatus for Relative Fluorescence Intensity Measurements

mirror and collimated onto a square-section quartz fluorescence cell or a square quartz dewar containing the cell. Fluorescence emitted at right angles to the incident beam passes through two baffles and a Corning filter and is recorded on a RCA No. 6199 photomultiplier tube. The output current of the phototube passes through a variable resistor shunted in parallel with a Rubicon galvanometer. Cells and dewar used in these experiments are shown in Figure 19.

The fluorescence intensity is proportional to the output of the photomultiplier. Intensity is recorded as the resistance of the shunt required to deflect the galvanometer a constant amount in each experiment. For resistors in parallel, the total current is related to the resistances by

$$I = V(1/R_1 + 1/R_2) \quad 5-3$$

In this arrangement V , the voltage across the circuit, is a constant. R_1 is the shunt resistance and R_2 the internal resistance of the galvanometer, a constant with a value of $11,000\Omega$. Thus the current I , proportional to the total fluorescence, can be obtained from the appropriate value of R_1 . In practice, since only ratios of intensities are of interest, V is eliminated and the ratio of quantum yields is simply equal to the ratio of the two values of the current, I .

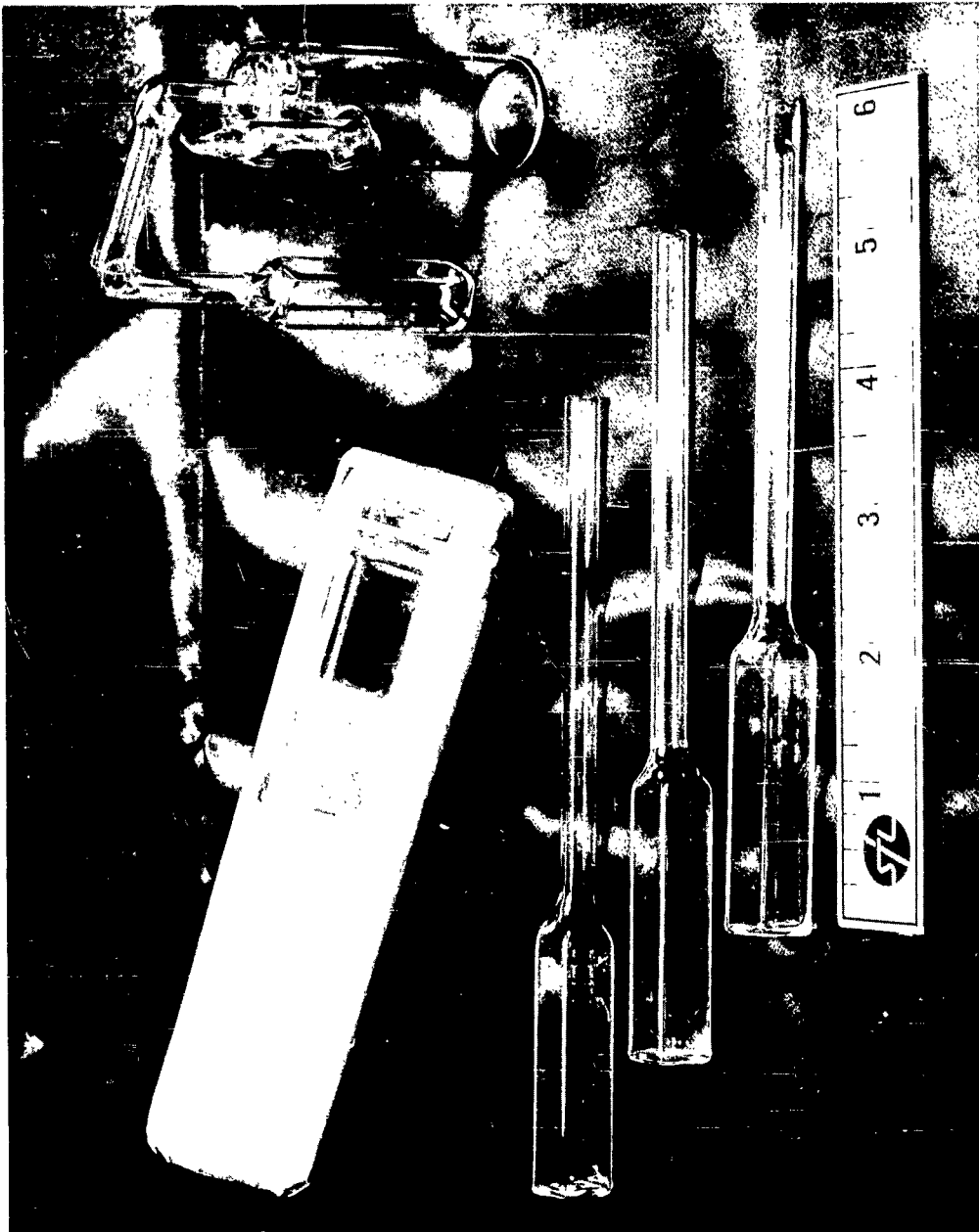


Figure 19. Square-Section Quartz Dewar and Cells

B. Quantum Yield Results

The technique of measuring quantum yields by the Weber-Teale method was developed by experimentally checking the literature values of quantum yields of several systems. The results appears in Table VI.

A survey of Table VI indicates that nearly the same quantum yield of fluorescence was obtained with and without using the rhodamine B quantum counter and that sufficiently good agreement was obtained with literature values. The systems in Table VI also nearly covered the possible range of quantum yields.

The quantum yields of fluorescence of rare earth chelate solutions at room temperature were subsequently measured (Table VII). Estimates of quantum yields at 77°K were obtained in several cases from quantum yield measurements at room temperature and from the relative fluorescence intensities at 77°K and 23°C.

The chelates appearing in Table VII are those which gave the highest quantum yield in solution at room temperature. The quantum yield of 0.32 for freshly diluted TbA₃ in 3 methylpentane is the highest value. However, an hour later the quantum yield of the solution was down to 0.23, which was close to the value of the quantum yield of 0.22 for an hour-old solution of TbA₃ in cyclohexane. This illustrates the rapid deterioration of fluorescence from low concentration (10^{-5} - 10^{-6} M) TbA₃ solutions as are employed for the WT method. The rapid deterioration of the dilute solution causes the measured value of the quantum yield of TbA₃ in toluene to be much lower when determined by the WT method than when determined by the BM method. Since, at the higher concentrations used in the laser experiments, deterioration is negligible, it is more appropriate to use the higher value, e.g., 0.32, for TbA₃ in 3 methylpentane. For EuB₃ in isopentane, the WT and the BM measurements agree fairly well. This shows that EuB₃ is more stable in dilute solutions than TbA₃.

Table VI

COMPARISON OF QUANTUM YIELD MEASUREMENTS
WITH LITERATURE VALUES (NONDEGASSED SOLUTIONS)

Fluorescent Molecule	Solvent	Quantum Yield at 23°C (STL Value)	Comments	Quantum Yield (Literature value)	Reference
Fluorescein	0.1N NaOH	0.97	Rhodamine detector used	0.93	24
Fluorescein	0.1N NaOH	0.90	Rhodamine detector not used	0.93	24
Quinine Sulfate	1M H ₂ SO ₄	0.52	Rhodamine detector used	0.55	24
Anthracene	Benzene	0.24	Rhodamine detector used	0.23	24,25,27
Uranyl Acetate	Water	0.032	Rhodamine detector used	0.04	24

Note: All the above measurements made by the WT technique.

Table VII
QUANTUM YIELDS OF FLUORESCENCE
OF CHELATES
(STL Values)

Chelate	Solvent	Quantum Yield at 23°C	Quantum Yield at 77°K	Method of Measure- ment	Wavelength of exciting light (mμ)
EuB ₃	Isopentane	0.022	0.13	WT	365
EuB ₃	Isopentane	0.020	0.12	BM	365
EuB ₃	Mineral Oil	0.022	-	EM	365
EuB ₃	Toluene	0.017	-	BM	365
EuB ₃	3-Methyl- pentane	-	0.12	-	365
EuA ₃	Toluene	0 ± 0.006	-	BM	315
TbB ₃	Mineral Oil	very low	20 fold increase from room temp.	-	365
TbA ₃	Toluene	0.09	-	BM	315
TbA ₃	Toluene	0.02	-	WT	365
TbA ₃	Cyclohexane	0.22	-	WT	365
TbA ₃	3-methyl- pentane (fresh solution)	0.32	-	WT	365
TbA ₃	3-methyl- pentane (hour-old solution)	0.23	0.60	WT	365
Eu(TTA) ₃	3-methyl- pentane	0.07	-	WT	365
Eu(TTA) ₃	Tetrahydro- furan	0.12	-	WT	365
Eu(TTA) ₃	Ethanol	0.066	-	WT	365

B-Benzoylacetonate

A-Acetylacetonate

TTA-Thienoyl trifluoro acetyl acetate

The high quantum yield of $\text{Eu}(\text{TTA})_3$ solutions should also be noted along with their excellent stability at high dilutions. Day-old solutions of $\text{Eu}(\text{TTA})_3$ gave the same quantum yield by the WT method as the freshly diluted solutions. The quantum yields of chelates are generally higher in hydrocarbon solvents than in polar solvents. However, $\text{Eu}(\text{TTA})_3$ is exceptional in exhibiting a significantly higher quantum yield in tetrahydrofuran than in 3-methylpentane.

Besides the various solvent systems recorded in Table VII, fluorescence intensities were measured in several other solvents. Usually, solutions in alcohols and ethers (e.g., dioxane) gave yields of less than 0.002 at room temperature ($\text{Eu}(\text{TTA})_3$ is exceptional in this respect). In addition to this, several chelates decomposed rapidly in these solvents. In general the order of decreasing intensity of any chelate in several solvents is, mineral oil > aliphatic hydrocarbons > glycerol > aromatic hydrocarbons > alcohols > ethers.

Several other chelates were investigated in solution. DyB_3 , SmB_3 , DyA_3 , SmA_3 and EuA_3 all had low yields in solvents tested. TbB_3 , in contrast to TbA_3 , had only a weak emission, even in mineral oil, at room temperature. However, at the temperature of dry ice (-80°C), TbB_3 had a bright emission and at 77°K it had increased to at least 20 times its value at room temperature (cf., Table VI).

Quantum yield measurements of chelates in many solvents were hampered by decomposition at concentrations below 10^{-5}M . One notable exception to this general rule is $\text{Eu}(\text{TTA})_3$. This chelate appears to be stable in many solvents even at concentrations approaching 10^{-6}M . This stability sets it apart from the other chelates tested. Its quantum yield is lower than TbA_3 (cf., Table VI). However, it is much more stable than TbA_3 at low concentrations. It also has a higher yield (0.066) in ethanol solution than any other chelate studied.

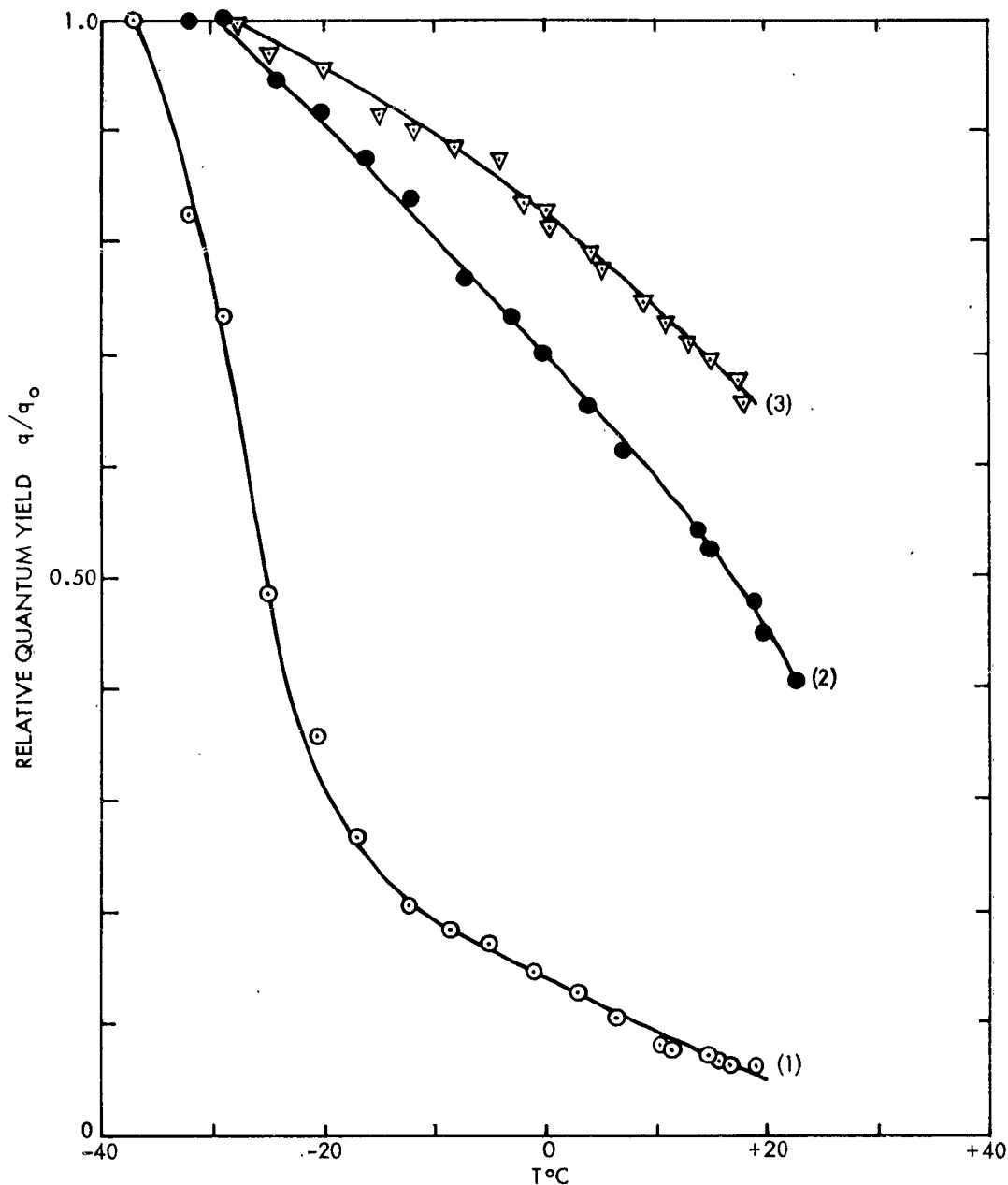
In some samples oxygen was removed by degassing. Since oxygen is a known quencher of both triplet and singlet states, one might expect an increase in light yield when oxygen is removed. No such effect was found. In some solutions removal of oxygen appeared to increase the light yield about 20%. However these effects were not reproducible and, generally, removal of oxygen had no effect on the fluorescence intensity.

In several systems the temperature was varied continuously from room temperature to about 233°K. In all cases the yield increases with decreasing temperature. Figure 20 gives the results of three measurements of typical systems. The increase of yield of TbB_3 by a factor of 14 is particularly notable. The temperature dependence of TbA_3 fluorescence was also investigated. This chelate had a fairly constant yield from 253°K to 77°K, indicating that it retains its maximum quantum yield up to quite high temperatures. Correlations of these readings with quantum yields are given in Table VII.

Conclusions

Of all the chelates tested, TbA_3 showed the highest yield. The remarkably high value of 0.32, even in solution at room temperature, makes it a prime candidate for a room temperature liquid laser. Because of the energy level scheme of Terbium, it also has a higher probability of 4-level operation at room temperature than Europium chelates. However, in order to pump TbA_3 efficiently, a quartz containing vessel and a quartz filler in the laser cavity must be used, since the majority of TbA_3 absorption occurs at wavelengths below the transmission limit of pyrex (ca. 3200Å). Narrow-bore quartz fillers must be specially made and are on order.

Both EuB_3 and Eu(TTA)_3 are also promising for laser action, especially at low temperature. Of the two, Eu(TTA)_3 has the higher quantum yield and a sharper emission spectrum. In addition, it has



VARIATION OF RELATIVE QUANTUM YIELD WITH TEMPERATURE IN VISCOUS SOLVENTS
 (1) TERBIUM BENZOYL ACETONATE IN MINERAL OIL
 (2) EUROPIUM BENZOYL ACETONATE IN MINERAL OIL
 (3) EUROPIUM BENZOYL ACETONATE IN GLYCERINE

Figure 20. Variation of Quantum Yield with Temperature

better stability and the position of its absorption band ($\lambda_{\text{max}} = 3410$) is more favorable for pumping. Both compounds have been examined for stimulated emission and the experiments are described in Section VIII. So far the results are somewhat equivocal.

C. Measurement of Fluorescence Lifetimes

An apparatus has been constructed for measurement of emission lifetimes down to approximately one millisecond (Figure 21). The luminescent specimen is placed in a clear quartz, flat bottomed Dewar, placed end to end with a RCA 6199 photomultiplier tube. Excitation light from a 100 watt high pressure mercury arc is passed through a quartz condensing lens and a photographic shutter onto the phosphorescent specimen. The high voltage on the cathode of the photomultiplier tube is automatically disconnected by means of a vacuum relay, to prevent overloading the phototube when the shutter is open. The shutter closes within 2 milliseconds and the vacuum relay reverses to connect negative high voltage to the photocathode within 3 to 5/^{milli}seconds after the shutter starts to close. After the shutter is closed a time-based, oscilloscopic display of the signal from the photomultiplier tube is photographed. The resulting oscillogram, which gives the time variation of luminescence intensity, is copied on graph paper. The luminescent lifetime may be obtained as the slope of the line formed by plotting the natural logarithm of luminescent intensity against time (Figure 22).

The above apparatus was constructed primarily for the purpose of studying the temperature dependence of the radiationless quenching of the phosphorescence of various aromatic compounds dissolved in plastic. The data in Table VIII, although only of marginal interest apart from the figures for benzophenone, illustrate the capability of the apparatus.

Quite recently we have used this apparatus for measuring the lifetime of TbA_3 . The fluorescence intensity^{vs.}/time and first order fluorescence decay plots for TbA_3 in 3-methylpentane appear:

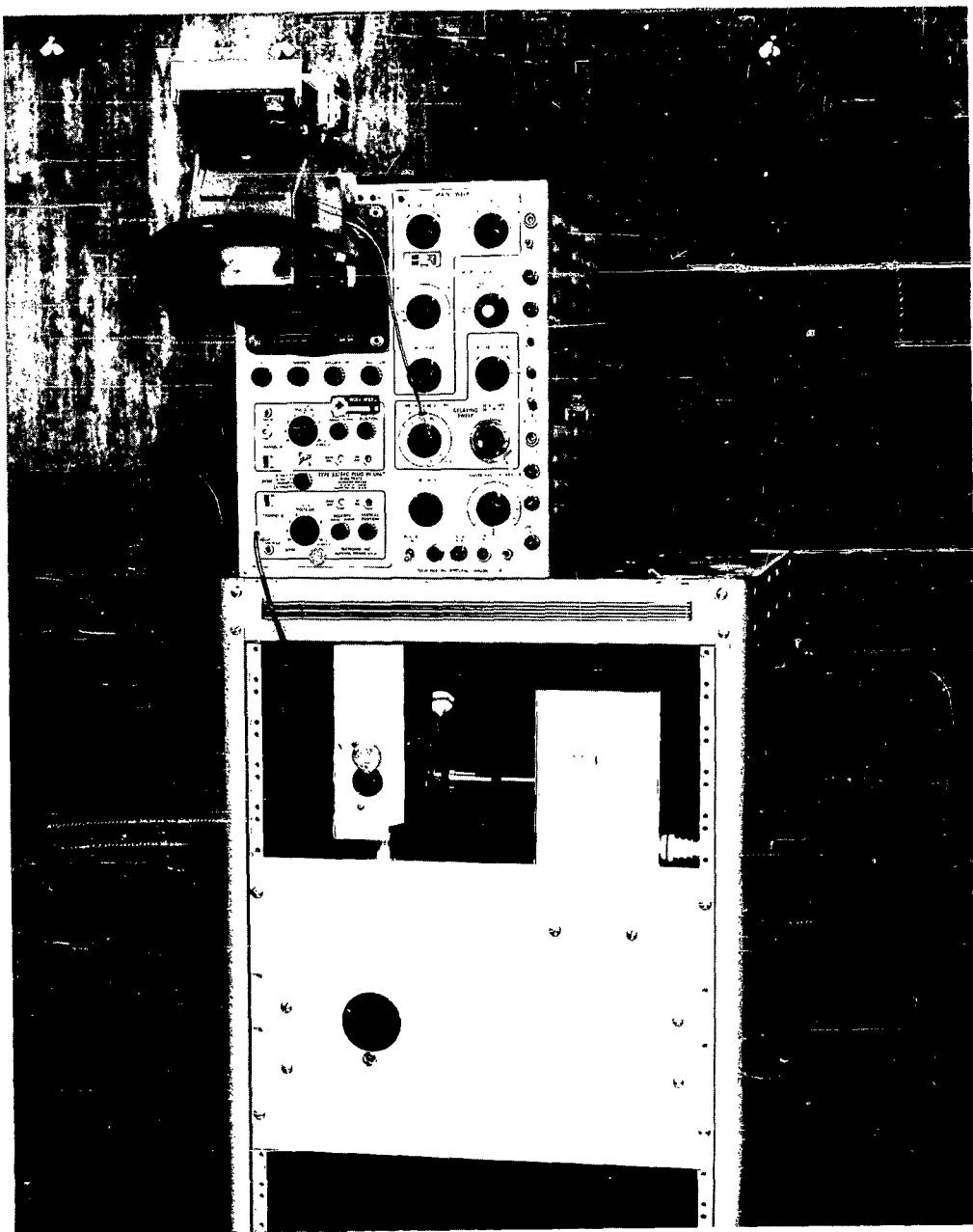


Figure 21. Fluorescence Lifetime Apparatus

Table III

Phosphorescence Lifetimes of Aromatic Molecules in
Cross-linked Polymethylmethacrylate (PMM) and EPA**

Compound	Phosphorescence in PMM Plastic			Phosphorescent Lifetimes in EPA at - 196°C. After McClure (15)
	Method of Cross- linking	Temperature in °C.	Lifetime in seconds (STL values)	
Picene	U.V.	-164	2.10	- -
		+23	1.0 - 1.2	
Triphenylene	U.V.	-196	14.1	- 15.6 - 16.2
		+23	4.2 - 4.9	
Chrysene	U.V.	-133	1.95	- 2.4 - 2.6
		+23	0.95 - 1.15	
Benzophenone	U.V.	-196	.0054 - .0058	- .006
		+23	.0018 - .0021	
Naphthalene	U.V.	-196	1.85	- 2.4 - 2.8 * (2.1 - 2.7)
		+23	1.25 - 1.45	
Phenanthrene	Benzoyl Peroxide	-150	3.2	- 3.1 - 3.4
		+15	1.8	

*STL Value

**5 parts ethyl ether, 5 parts isopentane and 2 parts ethanol
by volume.

in Figure 22 . The resulting lifetimes of TbA_3 in liquid solution at 23°C and in 3-methylpentane glass at 77°K are both nearly 1.0msec., which indicates that there is probably no increase of the radiationless quenching of excited terbium atoms between 77°K and 23°C .

Fluorescence lifetimes of several other rare-earth chelates have been kindly supplied by Freeman and Crosby (28). These are summarized in Table IX . Measurements were made using a micro-second flash apparatus. The decay times given are accurate to $\pm 1\mu\text{sec}$ or better.

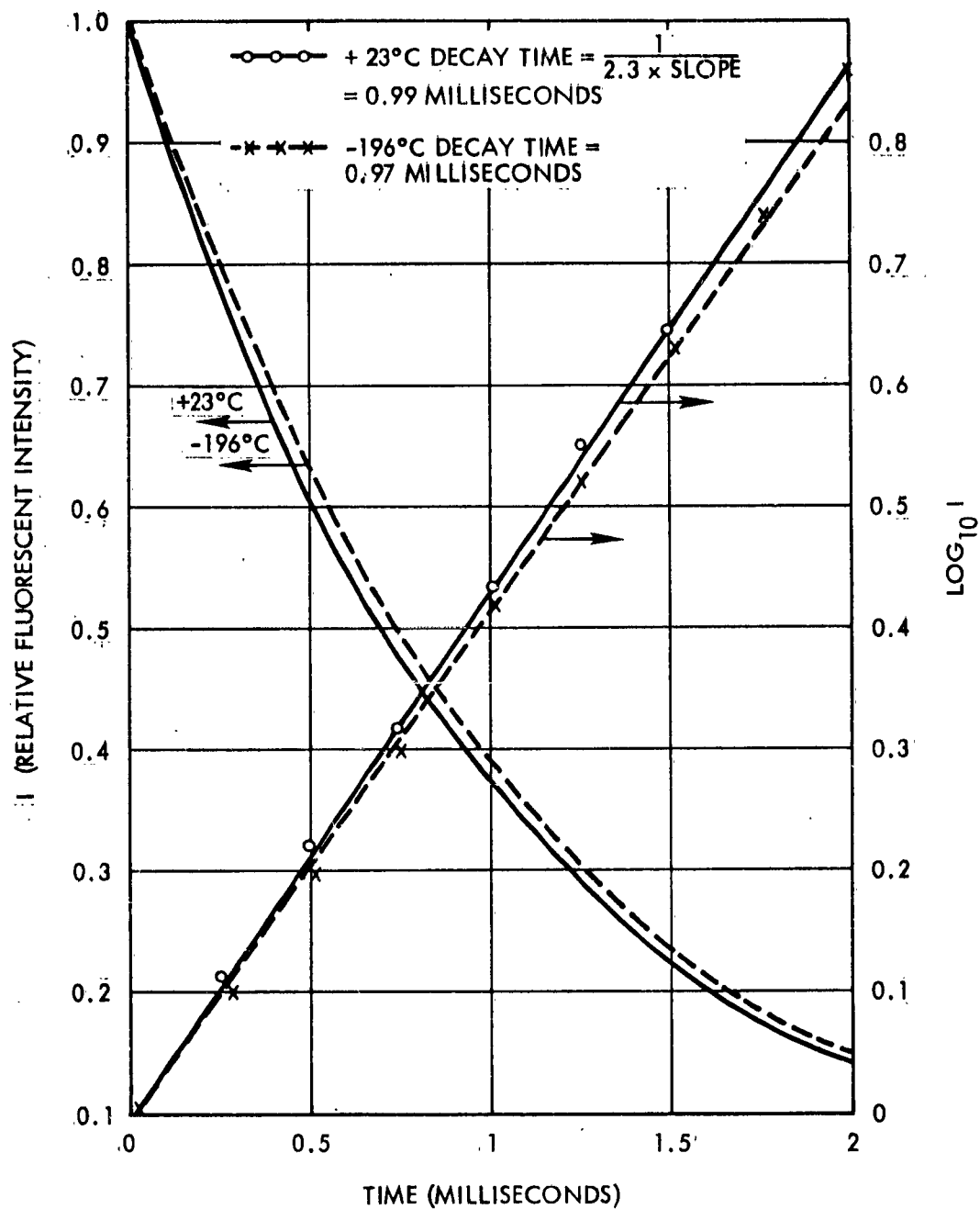
Figure 22. Fluorescence Lifetime Plot for TbA_3

Table IX

EMISSION LIFETIMES FOR VARIOUS RARE-EARTH CHELATES

Compound	Medium	Wavelength in Å	Mean Lifetime in μsec	
			At 77°K	At 298°K
$\text{EuB}_3 \cdot 2\text{H}_2\text{O}$	EPA	6100-6300	430	-
$\text{EuB}_3/2\text{H}_2\text{O}$	Solid Crystals	6200	466	311
EuD_3	EPA	6100-6300	361	-
EuD_3	Solid Crystals	6110	475	80
$\text{TbB}_3 \cdot 2\text{H}_2\text{O}$	EPA	5450-5650	630	-
$\text{TbB}_3 \cdot 2\text{H}_2\text{O}$	Solid Crystals	5400	650	-
TbD_3	EPA	5450-5650	464 and 159 (two components)	-
$\text{SmB}_3 \cdot 2\text{H}_2\text{O}$	EPA	6340-6540	14	-
SmD_3	EPA	6340-6540	20	-
$\text{DyB}_3 \cdot 2\text{H}_2\text{O}$	EPA	5610-5810	12	-

Notes: (1) EPA = Glass of Ether:Isopentane:Alcohol, 5:5:2 by volume.

(2) Data in this table by courtesy of J. J. Freeman and G. A. Crosby (23).

VII. The Liquid Laser Test Apparatus

A. The Confocal Laser Cell

The first problem in the design and assembly of a low temperature Laser experiment is the mounting and alignment of the optical cavity in a configuration which will remain stable when cooled from room temperature to 77°K. Although the plane parallel mirror configuration is known to have a high mode selectivity, the alignment-problems are much more severe. Therefore, a confocal mirror system has been chosen here, since the desirability of optimizing the experiment in hopes of achieving success far outweighs secondary problems involving mode hopping, beam divergence and monochromaticity.

As shown in Figure 23, the low temperature Laser cavity consists of a brass jig one inch in diameter by five inches long having an alignment mechanism at one end. The focal length of the mirrors is 4.65cm and they are 9.3cm apart. The silver-coated confocal mirrors used presented a problem initially, owing to cracking of the glass blank at low temperatures and burning of the silver surface at high flash energies. The installation of multiple-layer dielectric mirrors on a fused quartz substrate has resulted in a trouble free cavity, since the quartz is thermally stable and the dielectric mirrors either transmit or reflect the incident radiation, the absorption being a small fraction of 1%. Dielectric coated mirrors of high reflectivity and which are not soluble in the organic solvents used in our work, have been obtained from Keim Mirror Inc. Mirrors with maximum reflectivity at 4450A (benzophenone) 5450A (terbium), 6250A (europium) and 6943A (ruby) are now on hand.

Several thick-walled cylindrical pyrex inserts with narrow axial bores of different diameter (Figure 23) make it possible to vary the diameter of the column of liquid laser solution over the range 1mm to 6mm.

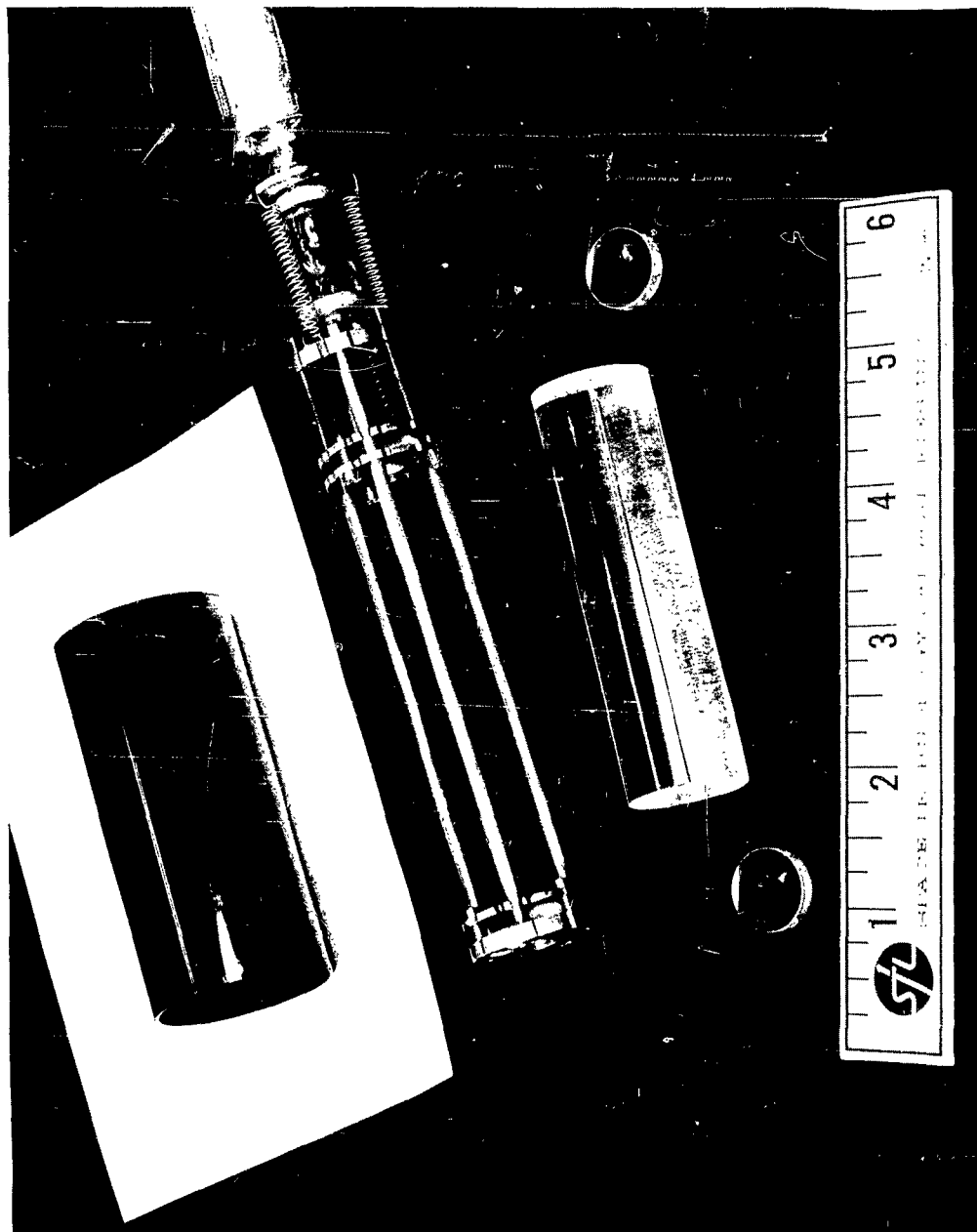


Figure 23. Close-Up of Confocal Laser Cell showing Mirrors,
Narrow Bore Adapter and Black-Glass Filter

In typical operation the mirrors are aligned at room temperature and the cell assembled in the pyrex reservoir as shown in Figure 23. The evacuated cavity is filled with the test solution and placed in a double dewar using liquid nitrogen in the outer dewar for cooling. The inner dewar contains a liquid such as isopentane or 3-methyl-pentane which remains liquid even when cooled to quite low temperatures. The laser cell, flash lamp and reflector are all immersed in the 3-methyl-pentane bath. Variation of the gas pressure in the inner dewar provides temperature stabilization at any given point down to 77°K . By a judicious selection of solvents one is able to obtain a viscous liquid or a rigid glass in the laser cell/ⁱⁿ the temperature range being studied.

Since the jig is aligned at room temperature, one may question whether or not the cavity is still in alignment at 77°K . In order to verify the procedures used in the study of liquid laser materials, an unsilvered ruby 0.20 inch in diameter and 2.0" long, was mounted in the cavity and flashed. The ruby was mounted inside the 6mm bore pyrex/about equidistant between the mirrors, with the aid of small coil springs, leaving a distance of 2.1cm between the flat ends of the ruby and the confocal mirrors. The system was flashed at 77°K under three conditions,

- (a) with the cell evacuated to a pressure of a few mm of Hg
- (b) with the cell filled with liquid
- (c) with the ruby frozen into a rigid organic glass.

Stimulated emission was readily observed under all three conditions. After several flashes with the frozen glass system, it was no longer possible to obtain laser action even at much higher flash energies. On removing the cell it was seen that many bubbles were present in the organic glass between the end of the ruby and the upper confocal mirror. This observation rules out the possibility that the uncoated ruby faces alone provided enough reflectivity for lasering and thereby confirms the good alignment of the confocal mirrors.

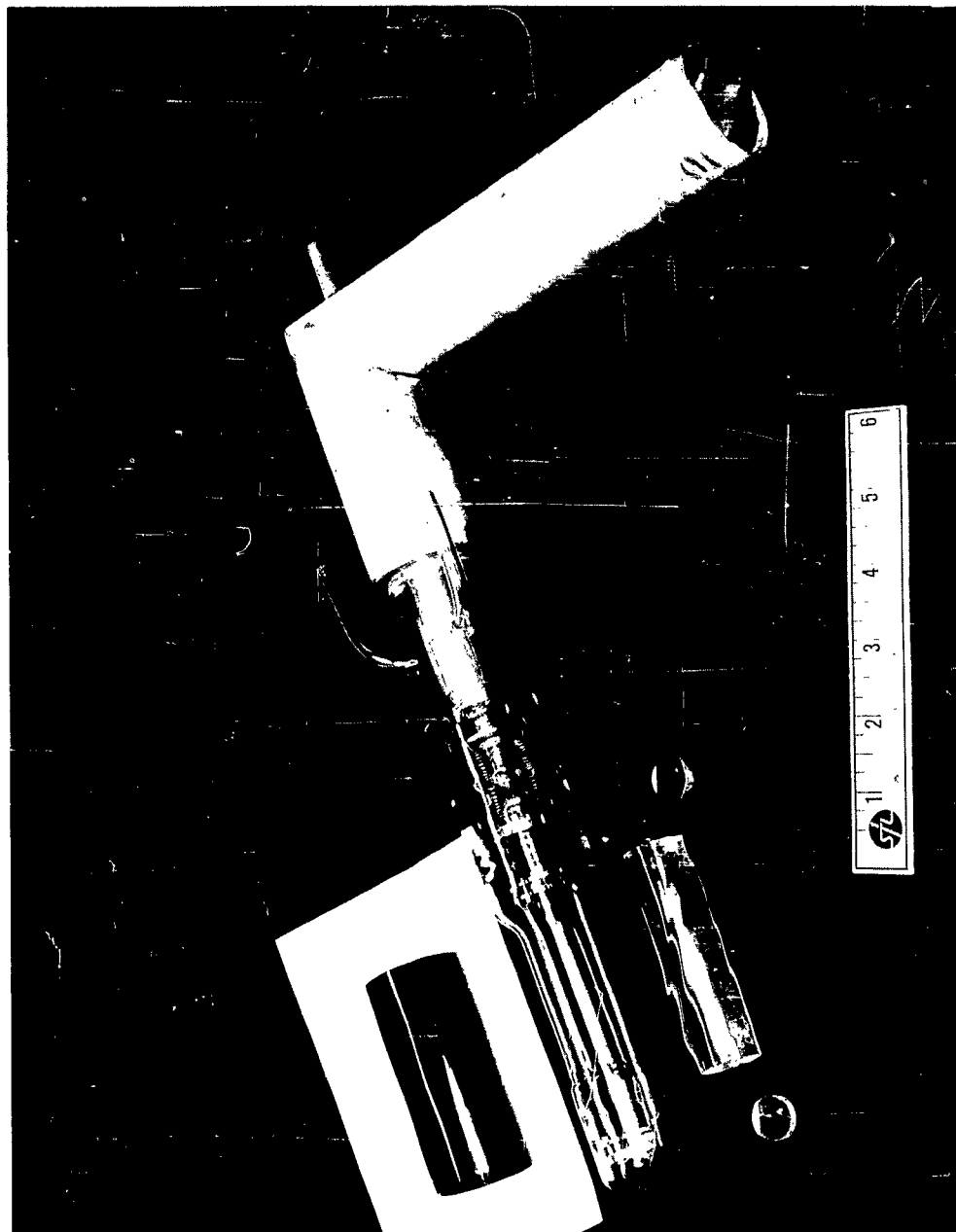


Figure 24. Confocal Laser Cell

B. Laser Detection System

A schematic diagram of the detection system is given in Figure 25. Fluorescence emission from the sample passes through the upper mirror and through a glass window into an evacuated tube. Since the evacuated tube with its end-window penetrates well under the surface of the liquid or frozen glass, it functions in a manner similar to a glass-bottomed boat, thus providing a clear optical path. In addition the evacuated tube provides heat insulation and prevents condensation of atmospheric moisture. In order to increase the signal to noise ratio, a narrow cone of light emitting from the center of the confocal cavity is selected by arranging several small apertures in the evacuated tube. After striking a 45° mirror the beam passes out of the evacuated tube through an inclined window to the entry slit of a 500mm focal length Bausch and Lomb grating monochromator. The confocal cavity and evacuated tube are shown in Figure 24 and the completely assembled apparatus in Figure 26. Usually the entry slit of the monochromator is set at 2 mm. By leaving the exit slit wide open the complete emission spectrum can be photographed. The exit slit is then narrowed down to select the band one wishes to study.

The fluorescence emission is monitored in three different ways:

- a. The integrated flash output is detected with a photocell and is displayed as trace A on the oscilloscope.
- b. The monochromatic emission of the compound under test is detected with a photomultiplier at the exit slit of the monochromator and is recorded as trace B on the oscilloscope.
- c. The exit beam from the monochromator is split with a partial mirror and the emission spectrum recorded on polaroid film with a dispersion of 5 Å/mm and total coverage of 150 Angstroms.

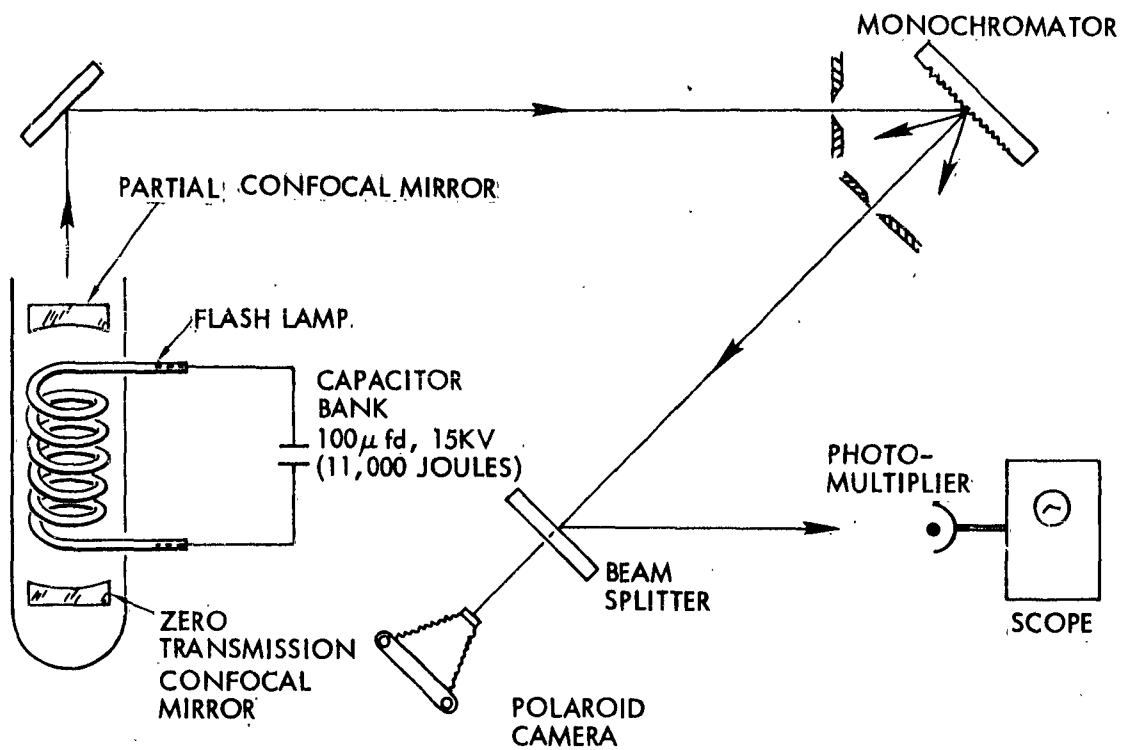


Figure 25. Schematic Diagram of Liquid Laser Apparatus

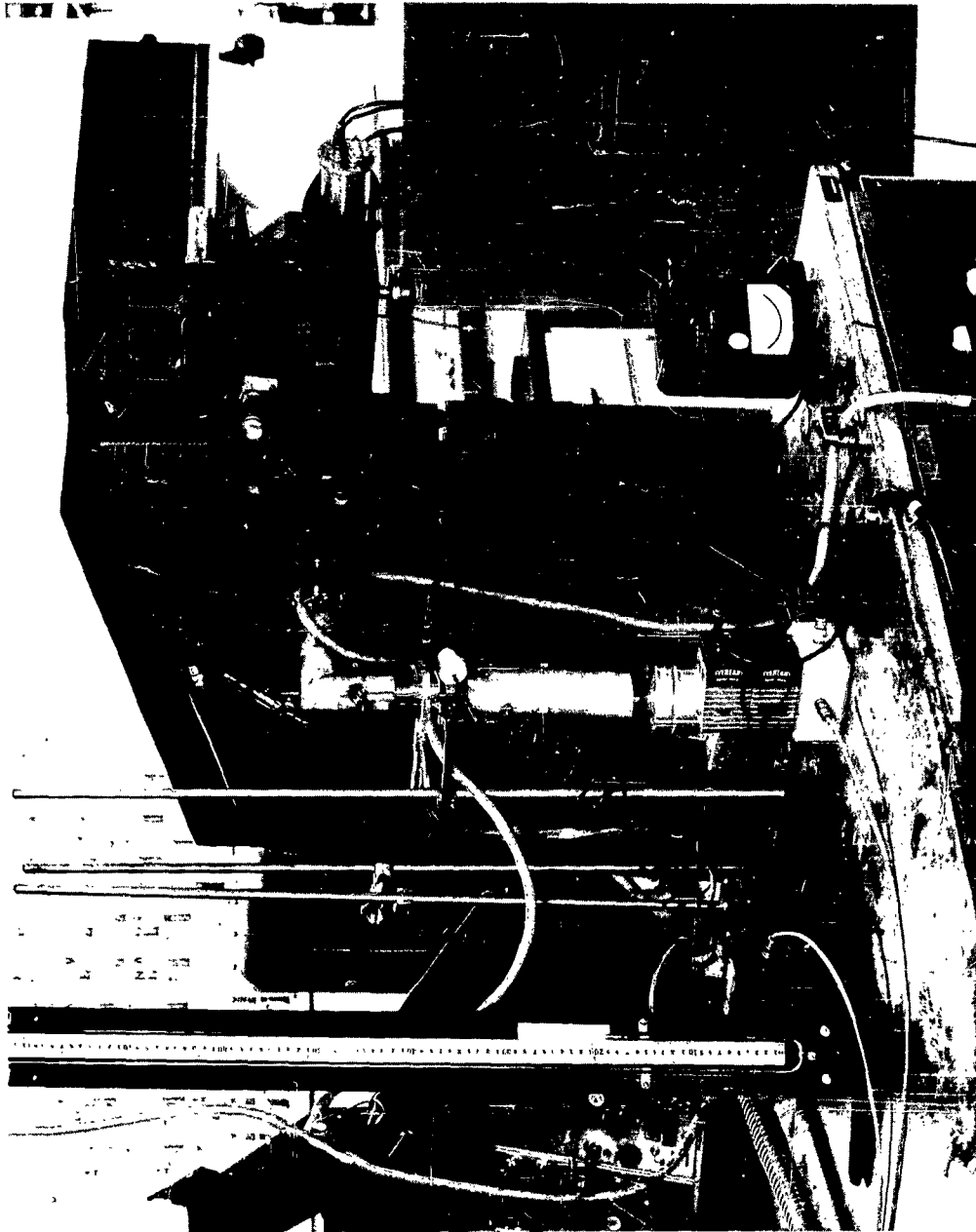


Figure 26. Overall View of Laser Apparatus

C. The Flash Apparatus

The flash apparatus used for laser experiments employs a 100 microfarad capacitor bank which may be charged to 16KV or 12,8000 joules. In typical operation, STL manufactured lamps are flashed between 7KV (2,500 joules) and 15KV (11,400 joules). The pulse width at 1/2 the peak intensity is approximately 500 microseconds. A GE type 7703 ignitron is used to hold off the applied voltage since the lamps fire spontaneously above 5KV.

A high energy helical quartz flash lamp, designed for low temperature experiments is shown in Figure 28. Several modifications were required in order to convert a normal or room temperature lamp to an efficient low temperature pumping source. When one looks at the optical efficiency of trying to pump a Laser with a flash lamp external to the dewar, it becomes immediately obvious that only a small portion of the input energy ever reaches the sample. Therefore, the experimental arrangement decided upon was to immerse the flash lamp in the liquid nitrogen or other low-temperature refrigerant. With this technique the flash lamp closely surrounds the Laser cavity, hence optimizing the optical coupling to the cavity. The first modification required is to convert the circuitry from the conventional trigger pulse mode of operation to a spark gap or ignitron hold-off circuit. This is necessary because of the electrical insulation properties of the liquid nitrogen bath, which prevents the trigger pulse from ionizing the lamp. In typical operation, potentials of from 7 to 15 kilovolts are held off with an ignitron and spontaneous breakdown of the lamp occurs when the switch is closed.

The conventional gas used for filling flash lamps, i.e. xenon, has been replaced with argon, since xenon is a solid at liquid nitrogen temperatures. In practice, a continuous flow of argon under a pressure of 2 to 20cm is passed through the lamp. In addition to providing stable firing characteristics and a

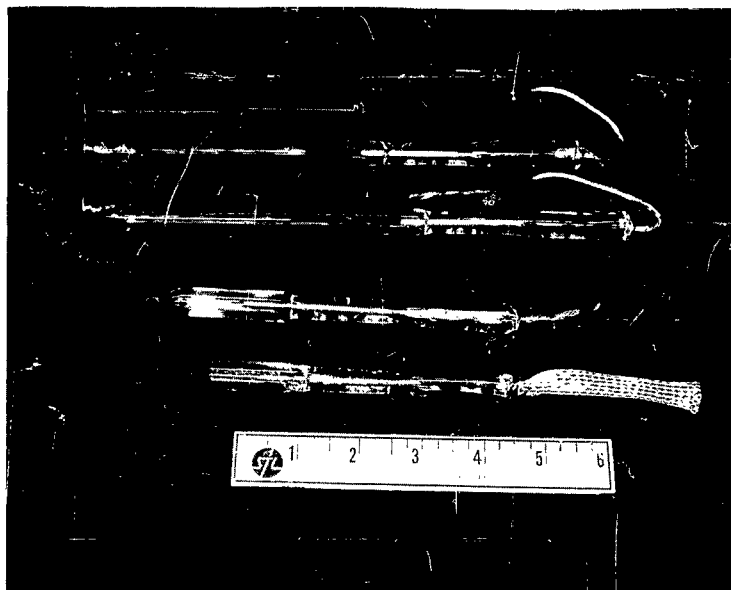


Figure 28. Flash-Lamp Electrodes

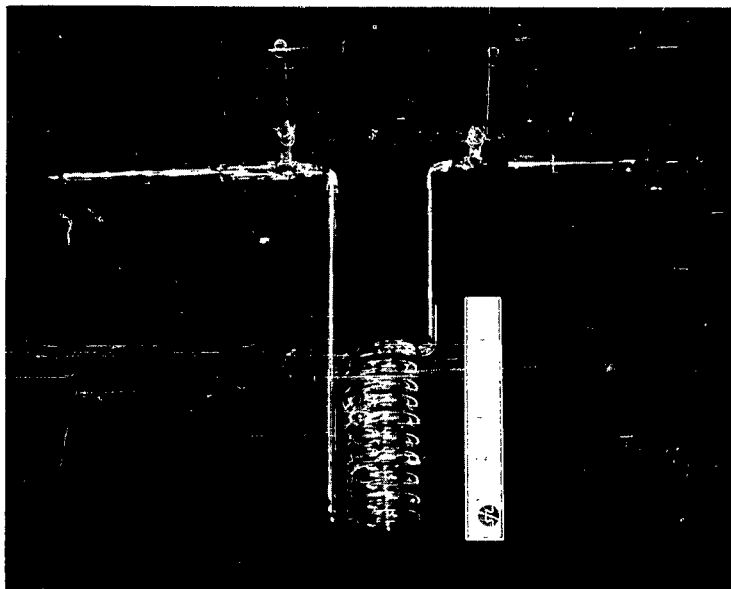


Figure 27. STL-made Helical 12,000 Joule Flash-Lamp

highly reproducible flash intensity, the circulating argon technique has eliminated pressure explosions at flash energies up to 11,400 joules. It also eliminates the problems associated with high-vacuum bake out and filling of conventional flash lamps.

Initially tungsten electrodes, sealed through quartz with a seal of metallic lead, were purchased from Thermal-American Fused Quartz Inc, Salem, New Jersey. However, it has since proved possible to fabricate similar electrodes quite satisfactorily from scratch in the STL Glass Shop. Figure 27 shows two commercial electrodes at the top and two STL electrodes below. The finished helical flash lamp, shown in Figure 28, has a total discharge path of about a metre. Similar lamps have been used satisfactorily at up to 11,400 joules per flash. Failure of the lamp may occur between 12Kv and 15Kv, but usually this entails a single fracture and the lamp is readily repaired. Breakage is probably associated with a shock-wave phenomenon; rarely do pressure explosions occur except at lamp pressures above 10cm of Hg. Lamps are usually operated in the pressure range 2 to 3cm.

VIII. Liquid Laser and Related Experiments

A. Concentration Considerations

In Section II-B we saw that an excess concentration of a few times 10^{-4} Molar in the emitting state should suffice for a typical rare-earth chelate to produce stimulated emission in a 10cm cell. Several uncertainties enter into the calculation. For one thing the true radiative lifetimes are not known accurately. For another, when dealing with a molecular band spectrum consisting of many bands, it is not at all obvious what value to use for the effective bandwidth in the calculation. We therefore decided to look for stimulated emission over a range of concentration from 10^{-4} Molar to 2×10^{-3} Molar.

In many cases the upper limit of concentration is bounded by the solubility of the chelate. However, another very important matter which must be taken into consideration is how far the pumping light penetrates into the sample. Recent theoretical work of Boyd and Gordon (29) has shown that the field of a confocal resonator is, in the lowest order mode, largely concentrated along the axis of the cavity. It is therefore especially important that population inversion be attained in the central portion of the sample. Since the peak extinction coefficient, ϵ_{\max} , for each of the chelates studied is of the order of 30,000, (See Section V.A) the optimum sample diameter for a concentration of 2×10^{-3} M (obtained by making the condition that the optical density not exceed unity) is 0.17mm. At a concentration of 10^{-4} M, the corresponding figure is 3.3mm. In practice, making the sample diameter as small as 0.17mm would introduce very severe problems of alignment. As a practical compromise, we have used one or other of two cylindrical pyrex inserts, one with a 6mm diameter and the other with a 3mm diameter. It would appear that, at the high end of the concentration range, only light towards the tail of the absorption curve would penetrate through to the centre of ^{the} sample.

However, one favorable factor which should not be overlooked is that, as population equality is achieved in the outer layers, the sample becomes transparent to the pumping radiation, which can then penetrate further into the sample. It is nevertheless true that a large fraction of the pumping radiation is wasted in the high concentration experiments.

B. Experimental Results

In Table X we summarize the systems that have been investigated for laser action to date. Experiments were done both in rigid glasses and in fluid solutions at low temperatures. Flash energies ranged from approximately 3000 to 10,000 joules. The majority of the experiments have so far yielded negative results. However, very recently, results suggestive of stimulated emission have been obtained for Europium Benzoylacetate (EuB_3) in a low temperature liquid. The EuB_3 was dissolved at a concentration of 10^{-3} Molar in the 2:1:2 Isopentane:Butanol:Propane mixture and flashed at a temperature of approximately 100°K . The results are shown in Figure 29. In each case the top exposure monitors the light output from the flash lamp. The bottom exposures show the emission from the sample displayed at two different amplifications. The time scale is $200\mu\text{sec}$ per scale division. Notice that in (a) and (b) the decay of the europium chelate emission closely follows that of the exciting flash. In (c), on the other hand, the decay curve is quite different in appearance and exhibits a definite spike which occurs just after the peak of the flash.

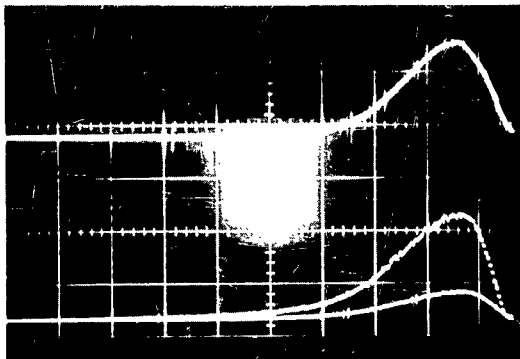
The exit slit of the monochromator in this experiment was set at 10mm. This means that a 50Å band centered at approximately 6130Å is being observed by the photomultiplier. This includes the strongest emission line of EuB_3 and two weaker lines. The rather low signal to noise ratio in the above trace could be due to this wide bandwidth. Reducing the bandwidth in an initial

Table X

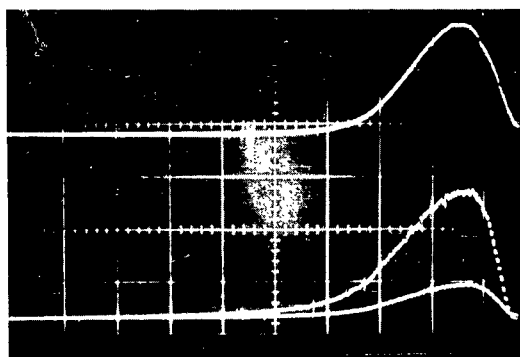
COMPOUNDS STUDIED FOR LIQUID LASER ACTION

Compound	Cell Diameter in cm	Molar Concentration	Solvent	Temperature	Glass (G) or Liquid (L)
Benzophenone	2.0	10^{-3}	3:1	77°K	G
TbD_3	2.0	10^{-4}	3:1	77°K	G
	2.0	10^{-5}	3:1	77°K	G
	ca.0.3	2×10^{-3}	Toluene	196°K	L
TbA_3	ca.0.3	2×10^{-3}	Mineral Oil-Propane	196°K	G
EuD_3	2.0	10^{-5}	7:1 IB	77°K	G
EuB_3	0.32	5×10^{-5}	3:1	77°K	G
	0.32	10^{-3}	7:1 IB	77°K	G
	0.32	2×10^{-3}	7:1 IB	77°K	G
	0.32	2×10^{-4}	7:3 IB	77°K	G
	0.32	10^{-3}	1:2:2 BIP	Approx. Temp. $90-150^{\circ}\text{K}$	L
	ca.0.3	5×10^{-4}	1:5:3:5 BIP		L
	ca.0.3	10^{-3}	1:1:3 BIP		L
$\text{Eu}(\text{TTA})_3$	ca.0.3	10^{-3}	1:2:2 BIP	$100-125^{\circ}\text{K}$	L
	ca.0.3	10^{-3}	1:2:2 BIP	$100-135^{\circ}\text{K}$	L
	ca.0.3	2×10^{-4}	1:2:2 BIP	$95-150^{\circ}\text{K}$	L
	ca.0.3	10^{-3}	1:2:2 BIP	$95-150^{\circ}\text{K}$	L
SmB_3	0.32	10^{-4}	7:1 IB	77°K	G

(a) 11Kv



(b) 12Kv



(c) 13Kv

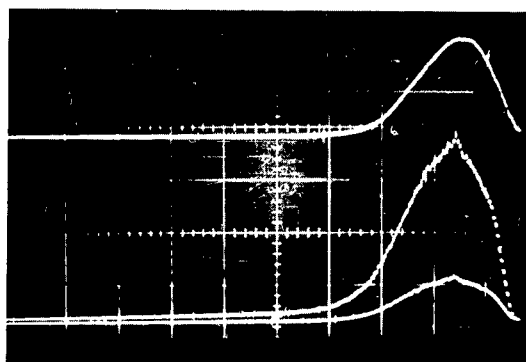


Figure 29. Emission from 10^{-3} Molar EuB_3 in low-temperature (ca. 100°K) IPB solution as a function of flash energy

series of experiments would, however, run the risk of missing something of interest.

The exposures shown in Figure 29 were Nos. 5, 6 and 7 in a series of 8 shots. Shots 1, 2, 3 and 4 were made at 8Kv, 9Kv, 9Kv, and 10Kv respectively. After shot 6 the cell was removed from the liquid nitrogen bath for inspection. Small bubbles were present in the sample column and the medium looked glassy. The solution was allowed to warm up to remove the bubbles. It was then replaced in the liquid nitrogen bath and flashed 2 minutes later at 13Kv to obtain the interesting result shown in Figure 26 (c). Immediately afterwards the cell was removed again and inspected. This time the material in the central column was definitely still liquid. In addition some small particles of carbon were present. The cell was allowed to warm up and then once again recooled and this time flashed at 14Kv. The trace obtained showed no spike, however, On inspection it was found that more particles of carbon were now present and the experiment was therefore terminated.

It is too early yet to know if the above result is an authentic observation of stimulated emission. More observations are needed to determine whether or not the result is reproducible. Several more experiments have been attempted but in each case bubbles or carbon particles have subsequently been found in the solution.

The formation of carbon particles presents some puzzling features. In some runs charring has been evident after the first or second flash. In others no carbon can be seen after seven or eight flashes of comparable energy. Recently experiments have been conducted in a bath of cold 3-methylpentane instead of liquid nitrogen, using a double dewar technique as outlined in Section VII. In this way the sample temperature can be controlled rather carefully. There is some evidence that photochemical decomposition

with the formation of carbon is more likely to take place when the sample is rigid glass or a very viscous liquid, than when it is a free-flowing liquid.

Very recently Lempicki and Samelson (30) have reported observation of laser action at 6129A for a low-temperature solution of EuB_3 . Details of their experiments are not yet available. However, it appears that, contrary to our earlier ideas, laser emission is more likely in a liquid solution than in a glass, probably because of the better optical quality of a free-flowing liquid. We have also observed a single very sharp spike during the decay of the emission from a $2 \times 10^{-4}\text{M}$ solution of $\text{Eu}(\text{TTA})_3$. Again, however, more experiments are needed before we can say whether or not the observation is authentic.

In conclusion we feel that, with most of the experimental problems now overcome, the program is on the verge of producing successful results. Now that the way has been pointed by the work of Lempicki and Samelson, it should be possible to obtain liquid laser action in a number of other chelates. With its higher quantum yield and better stability, the $\text{Eu}(\text{TTA})_3$ compound should soon yield successful results. Indeed there is a very recent report of stimulated emission for this compound in a narrow plastic fibre by Presley and Wolff (31). The other compound which is a prime candidate for laser action is TbA_3 , for which we obtained a quantum yield of 32% even at room temperature. If this compound is studied in a quartz apparatus it may well produce liquid laser action at room temperatures.

IX. Review and Recommendations for Future Work

A. Review of Liquid Laser Research

The objectives of this research program have been to study the optical properties of liquids and liquid solutions which appeared to have the greatest propensities for laser action. It is appropriate at this point to review the achievements of the present program and relate them to pertinent new developments by other research groups that have taken place during the past year. In this way we can obtain a perspective view of the field of liquid laser research which will be of great value in determining the course of future efforts.

The first report of laser action using organic materials was by Morantz, White and Wright (32,33) in January, 1962. These workers claimed to have observed stimulated emission for a number of aromatic ketones and hydrocarbons in frozen organic glasses at 77°K. However, inability to reproduce these results since then, both by the original authors and by independent workers, throws doubt on the veracity of this work. Furthermore, the reported thresholds were lower by several orders of magnitude than our calculations (Section II) would lead us to expect.

During the past year rare-earth chelates have been the preferred choice of most workers in the field. The present program has provided badly needed information on the fluorescence yields of several chelates, both in room-temperature liquids and in rigid glasses at 77°K (See Table VII). Of all the compounds studied, Europium thienoyl-trifluoro-acetyl-acetonate ($\text{Eu}(\text{TTA})_3$) and Terbium acetylacetonate (TbA_3) appear to be the most favorable. The europium compound has a yield of 12% in tetrahydrofuran at room temperature with peak emission in the red at about 6130Å. The terbium compound has the remarkably high yield of 32% in 3-methylpentane even at room temperature and, on cooling to 77°K, the yield increases still further to about 60%. The terbium

emission is strongest in the green at 5440Å (See Section V-B and Figures 10 and 11). In addition, Europium benzoylacetate (EuB_3) gives a yield of 13% in isopentane at 77°K but this falls to 2.2% at room temperature.

A high-intensity, 10,000 joule, laser test apparatus employing a confocal resonant cavity has been constructed and has been used for evaluation of the above compounds. For both europium compounds in low-temperature (100 - 150°K) liquid solutions, very recent experiments have yielded results which look like stimulated emission. However, without further experiments to check their reproducibility, it is impossible to know whether these represent authentic laser action or not. Experiments with TbA_3 in toluene at 196°K yielded negative results, but, since the main absorption bands of this compound lie below the transmission limit of the pyrex vessel used, the pumping conditions were very far from optimum. This compound warrants further study in a quartz vessel. It is perhaps the best candidate of all for liquid laser action at room temperatures.

Encouraging news has come very recently from two other groups. Observation of stimulated emission from $\text{Eu}(\text{TTA})_3$ in a 1/2mm diameter plastic fibre at 77°K has been reported by Pressley and Wolff (31) and stimulated emission from a liquid solution of EuB_3 at -130°C is reported to have been observed by Lempicki and Samelson (30). In view of the above observations, especially the latter, it appears that a low-temperature liquid, by reason of its lack of strain and consequent better optical quality, may be a better medium for laser action in chelates than frozen glasses.

B. Recommendations for Future Work

We feel that it is most unfortunate that the present program has been left unsupported at such a critical juncture in its development. The history of the laser field and scientific research generally has shown that, once one group has made a

breakthrough into a new area, new discoveries have followed rapidly from groups which have been pursuing parallel paths. The present program has accomplished a great deal of basic ground-work. The TbA_3 compound clearly should be investigated without delay, with its promise of extending laser action to 5440A and to systems which are liquid at room temperatures. A small additional investment of effort now will almost certainly yield a disproportionately high return in the way of useful results. Any one of the above observations provides good reason for continuation of the present work. Together they constitute an argument whose cogency is hard to deny. We therefore recommend the following,

1. Continue experiments on $\text{Eu}(\text{TTA})_3$ and EuB_3 in liquid solutions in the temperature range 77° to 150°K , with the object of obtaining reproducible observations of laser action.

2. Study the threshold for stimulated emission as a function of temperature, with the object of progressively increasing the temperature at which liquid laser action can be observed.

3. Using a quartz vessel, attempt to observe laser action at 5440A for TbA_3 , both at low temperature and in liquid solutions at room temperatures.

The above represents a minimum program. In addition, it is highly desirable that quantum yield measurements and other optical studies of new chelates be continued, in order more fully to exploit the potential versatility offered by chelate molecules in such important areas as,

4. Tuning the laser by chemical substitution and varying the solvent medium.

5. Improving pumping efficiencies by suitable choice of the chelating agent.

6. Making progress towards CW operation, by ascertaining how the quantum efficiency of fluorescence may be optimized as a function of rare-earth ion, chelating agent and solvent medium.

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